SEE
FOLLOWING
NOTE

VOIR
NOTE
CI-APRÈS

PARTS OF THE ORIGINAL DOCUMENT

ARE OF POOR REPRODUCTIVE QUALITY

CERTAINES PARTIES DU DOCUMENT ORIGINAL

SONT DE PIÈTRE QUALITÉ DE REPRODUCTION

National Research Council Canada
Conseil national de recherches Canada

Safety Guide for Hydrogen

Hydrogen Safety Committee

Canada

NRCC 27406

88-03215/

NATIONAL RESEARCH COUNCIL
HYDROGEN SAFETY COMMITTEE

SAFETY GUIDE FOR HYDROGEN

BY

K.M. KALYANAM, PROGRAM MANAGER
INDUSTRIAL GROUP
THE INSTITUTE FOR HYDROGEN SYSTEMS
AND
D. ROBERT HAY
TECHNICAL DIRECTOR
HYDROGEN INDUSTRY COUNCIL

1987

Copyright 1987 by the
National Research Council of Canada

ISBN 0-660-12529-3 (English)
ISBN 0-660-92092-1 (French)

Copies of the publication may be obtained by mailing the appropriate remittance (cheque or money order made payable to the Receiver General of Canada - credit CNRC, to:

Publications Sales and Distribution Office
National Research Council
Ottawa, Ontario
K1A 0R6

Price: $12.00

DISCLAIMER

The authors, the Institute for Hydrogen Systems, the National Research Council and the Hydrogen Industry Council disclaim any liability for damages arising out of reliance on material contained in this Safety Guide.

ACKNOWLEDGEMENT

The authors appreciate the collaboration of the members of the National Research Council Hydrogen Safety Committee in providing assistance and guidance in compiling this document. In particular, they would like to thank Mr. Graeme Hayward, the Chief Operating Officer of the Institute for Hydrogen Systems and Mr. Don Kirkwood, the NRC Hydrogen Safety Committee member from the Linde Division of Union Carbide Canada Limited, for their valuable input and review of the document.

This document was funded by the Institute for Hydrogen Systems, the National Research Council and the Hydrogen Industry Council. The project has been carried out in close collaboration with the NRC Hydrogen Safety Committee consisting of the following members from government, industrial and research organizations:

- Mr. L. Gardner, National Research Council
- Dr. D. Robert Hay, Hydrogen Industry Council
- Mr. G.W. Hayward, Institute for Hydrogen Systems
- Mr. D. Kirkwood, Union Carbide Canada Limited
- Mr. R.E. Knowlton, Chemetics International Inc. (C.I.L.)
- Dr. H. Tam, Atomic Energy of Canada

This document was reviewed by the Hydrogen Industry Council Safety Committee comprising Dr. D. Robert Hay, Technical Director of the HIC, Dr. Gerald Crawford of Electrolyzer Inc., and Mr. James Sprague of Canadian Liquid Air.

ABSTRACT

Hydrogen has been successfully and safely handled in the industry for many years. The safety aspects of hydrogen are intimately related to the specific applications. New processes and new uses of hydrogen may pose new safety hazards that must be dealt with as they arise. This document, "Safety Guide for Hydrogen", outlines the general areas where the unique properties of hydrogen combine to create potential hazards, and the various techniques and methods commonly practised in industry for the identification, analysis, assessment and avoidance of hazards.

The availability of the document in this form demonstrates that industrial hydrogen process development has proceeded with due consideration to, and integration of the valued societal perspectives, expectations and requirements regarding safety.

EXECUTIVE SUMMARY

Hydrogen has been successfully and safely handled in the industry for many years. Hydrogen is a feedstock in the process industry. It is already the accepted fuel of the aerospace industry. Thus, the handling of large quantities of hydrogen in industry is essentially routine and no major problems are anticipated with its increased use in industrial processes.

The industrial hydrogen systems have, so far, been in the hands of hydrogen specialists, and as a result have been insulated from public attention. New processes and new uses of hydrogen, however, may pose new safety hazards that must be dealt with as they arise. One of the possible new uses of hydrogen is as a replacement fuel in all the major fuel markets - industrial, commercial, transportation and residential. Considerable safety analysis is in order prior to the wide spread use of hydrogen in transportation - particularly in highway vehicles, where personnel exposure is maximum and fuel handling procedures are most difficult or impossible to enforce. Thus, future development plans for the hydrogen industry in the above market sectors will increase the use of hydrogen, and will move hydrogen technologies closer to the public. Handling of hydrogen safety will be open to scrutiny by local interest groups in communities surrounding projected plant sites, organized labour, government ministries, and other professional and public interest groups. Importantly too, the media will mount a close watch for the potential for controversy, and safety is one of the most volatile of controversial issues.

Over the last century, as knowledge and social awareness of safety have expanded, society's perception of responsibility for human safety has become more demanding. Although hydrogen has been handled safely in industrial processes for decades, it is desirable to communicate to the professional, as well as the public, that the developments in the hydrogen industry have not proceeded without integrating the valued societal perspectives regarding safety that have been expressed and anticipated. It is equally important to convey to the public that unnecessarily strict regulation or expensive litigation proceedings stand to stifle the development of the hydrogen industry, and thus make the unique advantages of hydrogen unavailable to society.

This document, "Safety Guide for Hydrogen", addresses these objectives by providing a valuable guide to the present and future producers, handlers (storage and transport) and users of hydrogen, as well as designers of hydrogen systems, in matters of safety, without resorting to specific applications. The document outlines:

- the unique properties of hydrogen that combine to create potential hazards;
- the analytical techniques developed by the process industry to systematically and efficiently identify and evaluate prospective hazards, so that appropriate counter-measures can be implemented; and
- the regulations, codes, standards and industrial practices developed through years of experience in producing and handling hydrogen, and adopted by the industry for avoiding hazards.

The information contained in this document is intended to assist the scientific community in meeting safety obligations, both professional and in relation to the public. The document also demonstrates that public concerns, expectations and requirements regarding safety are being addressed.

TABLE OF CONTENTS

Page

1. HYDROGEN SAFETY

1.1 Introduction 8
1.2 Hydrogen Safety- Public Perspectives 9
1.3 Evolving Hydrogen Safety Requirements 10
1.4 Safety Guide for Hydrogen 12

2. INHERENT RISKS ASSOCIATED WITH HYDROGEN

2.1 Introduction 13
2.2 Hydrogen Properties and Hazards 13
2.3 Classification of Hydrogen Hazards 17
  2.3.1 Leakage/Spillage 17
  2.3.2 Combustion 18
  2.3.3 Detonation 22
  2.3.4 Reactions with Oxidants, Halogens and Metals 24
  2.3.5 Metal Embrittlement 24
  2.3.6 Asphyxiation 33
  2.3.7 Cryogenic Hazards 33

3. RISK AVERSION METHODS 38
3.1 Compliance with Codes, Standards and Guidelines 39
3.2 Quantity Limitation 40
3.3 Location and Separation of Equipment 40
3.4 Control of Hydrogen Accumulation within Enclosures 49
3.5 Exclusion of Air 49
3.6 Elimination of Ignition Sources 50
3.7 Leakage Detection and Control 52
3.8 LH2 Spill Containment 53
3.9 Instrumentation 53
3.10 Safety Reliefs 54
3.11 Safe Venting and Disposal 55
3.12 Fire Detection, Control and Extinguishment 57
3.13 Selection of Proper Materials of Construction 58
3.14 Cryogenic Precautions 60
3.15 Hazard Identification and Assessment 61

4. CODES, STANDARDS, REGULATIONS AND RECOMMENDED PRACTICES 63
4.1 Hydrogen Codes, Standards and Regulations- U.S.A. 64
  4.1.1 Hydrogen Storage 65
  4.1.2 Hydrogen Distribution/Transmission 65
  4.1.3 Hydrogen Transportation 66
4.2 Hydrogen Codes, Standards and Regulations- Canada 67

Page

5. HAZARD IDENTIFICATION AND EVALUATION (HAZOP & HAZAN) 84
5.1 General Approach to Hazard Identification 85
5.2 Analysis and Assessment of Hazards 88
5.2.1 Failure Analysis 89
5.2.2 Fault Tree Analysis 89
5.2.3 Hazard Analysis, or Hazan 90
5.2.4 Limitations of Hazop and Hazan

6. REFERENCES 92

7. APPENDICES

Appendix A- Properties of Hydrogen, Methane and Gasoline 96

Appendix B- Hydrogen Leak and Fire Detection Techniques 99
Appendix C- Bibliography 104

1. HYDROGEN SAFETY

1.1 INTRODUCTION

The hydrogen industry has been active successfully and safely for many decades. During this time, industrial systems have been in the hands of hydrogen specialists and as a result have been insulated from public attention. Development plans for the hydrogen industry, however, will increase the usage of hydrogen and move hydrogen technologies closer to the public. Handling of safety will be open to scrutiny by local interest groups in communities surrounding projected plant sites, organized labour, government ministries, and other professional and public interest groups. Importantly too, the media will mount a close watch for the potential for controversy and safety is one of the most volatile of controversial issues.

The hydrogen industry is favoured in that it is not pursued by the stigma of latent health or environmental effects that follows other industries which deal with many other hazardous substances. In fact, hydrogen has substantial positive appeal from the environmental point of view. Resources, therefore, can be focussed on technological design and risk assessment methodologies rather than the more nebulous effects studies that have plagued the nuclear and asbestos industries, to name two, with uncertain and unusable decision information. On the other hand, the occurrence of large-scale industrial disasters in Mexico, India and Great Britain in recent times and the subsequent saturation coverage in the media has raised public awareness of the dangers of highly explosive substances. This state of awareness should be addressed carefully in safety design and communication.

Unnecessarily strict regulation or expensive litigation proceedings stand to stifle the development of hydrogen industry and thus make the unique advantages of hydrogen unavailable to the public. Communication of an awareness of societal values and perceptions of risk must be initiated on the professional level and pursued in relations with concerned social actors and the public at large.

1.2 HYDROGEN SAFETY - PUBLIC PERSPECTIVE

Over the last century, as knowledge and social awareness of safety have expanded, society's perception of responsibility for human safety has become more demanding. The long, hard debate over safety in nuclear technologies has had a large impact on societal awareness of the dangers of high risk industries. The aforementioned front page explosive disasters in Mexico and Great Britain and the chemical containment breach in Bhopal, India have sparked a general societal awareness of just how close high risk technologies are to the public. The last decade has also, however, provided valuable experience in efficiently evaluating acceptable levels of safety and communicating to the public that safety is well in hand.

The Clean Air Act in the United States provides an example of the institutionalized treatment of health and safety in a social system closely related to that in Canada. In the determination of primary and secondary air quality standards (i.e., the protection of human health and the protection of the environment, respectively), economic costs are not allowed to be considered. This is a direct reflection of the extent to which safety concerns can activate public awareness to influence the regulatory process.

A major development that has emerged through the years of safety debate has been the successful participation of concerned social actors in the determination of safety policy. In many cases, expensive, time-consuming litigation has sometimes proven politically necessary; but moratoria on development, and the financial cost of this approach to reassuring the public of the safety of large scale industrial projects is inefficient and may be unnecessary from industrial, governmental and societal standpoints. As an alternative, industry must find ways to communicate to the concerned actors and the public not only the social benefits of development, but also a satisfactory reconciliation of societal perceptions of risk and concerns for safety.

The necessity for a new approach to introducing high risk technologies to the public was highlighted by the litigation breakwater that stalled the nuclear power industry. One of the major oversights of the nuclear power industry was that it did not actively attempt to communicate to the public that its treatment of safety issues reflected societal perceptions and concerns of the inherent risks of nuclear power, in addition to purely technical requirements perceived by the engineering community.

The simple concept of "safety first" is the basis of a successful approach to public confidence in hydrogen safety. The following initiatives are fundamental:

- industrial self-examination from both technological and sociological perspectives;
- awareness of contemporary societal perceptions of risk and individual concerns for security;
- exhibition of leadership in moral judgements;
- exhibition of co-operation and leadership within the regulatory and code setting communities;
- communication of the industry's dedication to the improvement of safety.

Although hydrogen has been used in industrial processes for decades, it is desirable to convey to both current and new users of hydrogen guidelines for the safe production, handling and use of hydrogen in this evolving social context. At the same time, it is equally desirable to convey to the public that adequate means are available and enforced to meet its expectations for safety of hydrogen systems.

1.3 EVOLVING HYDROGEN SAFETY REQUIREMENTS

Hydrogen has been used in large quantities in the petroleum refining, chemical, petrochemical and synthetic fuel industries for decades. Thus, the use of hydrogen in industry is essentially routine and no major problems are anticipated with its increased use in industrial processes. The electrical utility industry has also successfully used hydrogen gas to cool the rotor and stator coils in large turbine-generators for more than forty years. Hydrogen is already the accepted fuel of the aerospace industry and has been safely handled in large quantities. Preliminary safety analyses of hydrogen-fuelled aircraft for military and civilian applications have been in progress and the hazards associated with the use of hydrogen as a military fuel have been reviewed (1, 2, 33, 34).

New processes and new uses of hydrogen, however, may pose new safety hazards that must be dealt with as they arise. One of the possible new uses of hydrogen is as a replacement fuel in all the major fuel markets-industrial, commercial, transportation and residential. Hydrogen has not been used extensively in commercial applications, although it has been successfully piped cross-country as a compressed gas in a few locales. Excluding a few demonstration projects with automobiles, trucks, buses and airplanes, hydrogen is a relatively untried fuel in the transportation market. Considerable safety analysis is in order prior to the wide spread use of hydrogen in transportation-particularly in highway vehicles where personnel exposure is maximum and fuel handling procedures are most difficult or impossible to enforce. Hydrogen can also be used to supply residential fuel needs, but from a safety perspective there are a number of significant concerns related to the problems of gas leakage, detection and the potential severity of explosions of hydrogen-air mixtures in confined or partially-confined spaces. However, hydrogen-enriched gases (coal gas, town gas, producer gas, etc.) were successfully used in European countries to satisfy residential fuel needs throughout much of the last century.

A detailed safety analysis covering the use of hydrogen in the potential future market areas is needed. Credible accidents must be postulated, meaningful hazards data must be developed and hazard analysis and assessment must be carried-out. The safety aspects of hydrogen are intimately related to the specific application and the postulated accident criteria. This document presents some of the safety hazards associated with hydrogen, without resorting to specific applications and specific accident criteria.

1.4 SAFETY GUIDE FOR HYDROGEN

This document, " Safety Guide for Hydrogen " is intended to provide a valuable guide to the present and future producers, handlers (storage and transport) and users of hydrogen, as well as designers of hydrogen systems in matters of safety. It identifies those general areas where the unique properties of hydrogen combine to create potential hazards and effective methods to ensure that safe procedures are followed.

The purpose of this document is to clearly demonstrate that industrial hydrogen process development has not proceeded without integrating the valued societal perspectives that have been expressed and has anticipated the directions that they will take in the future. It addresses these objectives by outlining:

- the inherent properties of hydrogen which give rise to risk
- the nature of the risks produced by certain properties
- the methods available for risk aversion
- a number of the specific risk aversion methods used in practice
- the various techniques available for hazard identification, analysis and assessment, in order to propose and adopt the appropriate risk aversion methods in hydrogen systems.

This Guide is intended for the use of the scientific community and for providing them with assistance in meeting safety obligations, both professional and in relation to the public. The information contained in this document will also provide other readers with the assurance that general societal expectations and requirements for safety are being addressed.

2. INHERENT RISKS ASSOCIATED WITH HYDROGEN

2.1 INTRODUCTION

A comprehensive understanding of the safety-related properties of hydrogen and their contribution to potential hazards, as well as the application of known safety technology, is essential to ensure safe design, handling and operation of hydrogen facilities. This section discusses the inherent hazards or hazardous conditions represented by the various physical and chemical properties of hydrogen. It is designed to familiarize the reader with the known risks associated with hydrogen and the safety initiatives which are and can be taken to minimize or eliminate the risks involved.

2.2 HYDROGEN PROPERTIES AND HAZARDS

A brief review of the extensive literature on hydrogen indicates the following:

- It is the lightest of all elements;
- It is colourless, odourless, tasteless and non-toxic;
- It is a flammable gas which burns with a colourless flame in the absence of impurities.
- It is similar to other fuels in many respects. However, it does have certain unique properties that makes it either more or less hazardous.
- The actual contribution of a property to a particular hazard depends strongly on the specific conditions under which hydrogen is confined and/or released.

The significant properties of hydrogen included in Appendix-A, and the related hazards have been analyzed and summarized by J.Hord (1), with a comparison to methane and gasoline to provide a perspective for the relative safety of hydrogen. The relevant physical and combustion-related properties of hydrogen that are of concern to safety are highlighted in Tables-2.1 and 2.2 respectively.

TABLE 2.1 PHYSICAL PROPERTIES OF HYDROGEN

PROPERTY	HYDROGEN*
Molecular weight	2.02
Normal boiling point (NBP), °C	-253
Critical temperature, °C	-240
Critical pressure, kPa	1300
Density of liquid at NBP, kg m^{-3}	70.8
Specific gravity of liquid (Water = 1.0)	0.07
Density of vapour at NBP, kg m^{-3}	1.34
Specific gravity of vapour (Air at 16°C = 1.0)	1.1
Density of gas, kg m^{-3}	0.0826
Specific gravity of gas (Air = 1.0)	0.068
Diffusion velocity in air, m sec^{-1}	0.02
Buoyant velocity in air, m sec^{-1}	1.2 to 9.1.
Heat of vaporization at NBP, kJ kg-1	446
Toxicity	simple asphyxiant

---

[*] Based on the para form

TABLE 2.2 COMBUSTION-RELATED PROPERTIES OF HYDROGEN

PROPERTY	HYDROGEN
Gross heat of combustion (Higher heating value), kJ kg^{-1}	141,800
Net heat of combustion (Lower heating value), kJ kg^{-1}	119,900
Flammability limits, vol. % in air	4.0 to 75.0
Detonability limits, vol % in air	18.3 to 59.0
Limiting oxygen index, vol. %	5.0
Minimum ignition energy, mJ	0.02
Hot-air ignition temperature, °C	671
Flame temperature in air, °C	2000
Radiative heat transfer from flame, %	17 to 25
Maximum safe gap, mm	0.08
Burning velocity in air, m/s	2.7 to 3.4
Detonation velocity in air, m/s	1480 to 2150
Energy of explosion, kg TNT/GJ	~ 160

2.3 CLASSIFICATION OF HYDROGEN HAZARDS

The chemical make-up of hydrogen gives it unique interactional qualities compared to other dangerous substances. On average, its properties do not make hydrogen any more, or less dangerous than, for example, methane or gasoline, since as in the case of all dangerous substances, hydrogen must be handled with due regard to its unique properties.

By definition, a hazard identifies a pending risk or peril. The known hazards associated with hydrogen can be classified under the following headings:

- Leakage/Spillage;
- Combustion
- Detonation
- Reaction with oxidants, halogens and metals;
- Metal embrittlement;
- Asphyxiation; and
- Cryogenic hazards.

2.3.1 Leakage/Spillage

The leakage/spillage of hydrogen is considered a potential hazard, since it may contribute to the existence of a combustible or explosive hydrogen-air mixture. Hydrogen, gaseous or liquid, is more difficult to contain than other fluids because of its low molecular mass and atomic radius. Hydrogen diffuses rapidly through porous materials and through some metals at red heat. A container that is airtight is not necessarily hydrogen-tight.

The rate of leakage flow of liquids or gases through leakage paths is an important matter of concern in evaluating fire hazards. The volumetric leakage rate is inversely proportional to the absolute viscosity or to the square root of the density. Using the data given in Appendix A, we can estimate the relative volumetric leakage rates of the NBP liquid fuels and of the gases at NTP. Under these conditions the volumetric leakage flow of liquid hydrogen will be 2.4 to 8.5 (viscous flow) times as large as liquid methane leakage and 3.1 to 15 (viscous flow) times as large as liquid gasoline leakage; volumetric leakage flow of hydrogen gas will be 1.3 (viscous flow) to 2.8 times as large as gaseous methane leakage and 0.6 (viscous flow) to 7.3 times as large as gasoline vapor leakage. Since care is usually taken to minimize fuel leaks, the viscous leakage flows are considered to have the greatest practical significance. Thus, it can be concluded that, in general, the rate of leakage of hydrogen through leakage paths such as cracked welds, improperly mated flanges, threaded fittings, damaged seals, etc., would be higher than it is for other fuels. It can also be concluded that liquid hydrogen is much more difficult to contain than liquid methane or liquid gasoline and that NTP gasoline vapours are more difficult to contain than either NTP hydrogen or NTP methane. In spite of the unfavourable leakage characteristics, industry has proven that both liquid and gaseous hydrogen can be safely and easily contained.

2.3.2 Combustion

The most widely recognized hazard in handling hydrogen is that of unwanted combustion. For a combustion hazard to exist, a flammable mixture of the hazardous fluid and air, and an ignition source must be present.

Flammability: Three properties which influence inflammability are buoyant velocity, diffusion velocity and flammable limits. Hydrogen's values for each of these properties make it more flammable than both methane and gasoline. The flammability limits of hydrogen-air and hydrogen-oxygen mixtures depend on initial pressure, temperature, and water vapour content. In dry air at atmospheric pressure, the lower limit is 4.1% hydrogen, and the upper limit is 74.2% hydrogen by volume. In dry oxygen at atmospheric pressure, the lower limit is 4.7% hydrogen, and the upper limit is 93.9% hydrogen by volume. The rate at which the gas mixes with air is indicated by the diffusion velocity and the buoyant velocity. Hydrogen escaping into a confined space will reach its lower flammable limit of 4% by volume 3.78 times faster than methane will reach its 5.3% threshold. The higher diffusion and buoyant velocities allow hydrogen to spread quickly through the surrounding environment, thus reaching combustible concentrations more quickly and covering a larger area with combustible substance. However, the energy contained within the confined space that would be released in a fire or explosion is only one quarter of the energy of a 5% methane-air mixture. Without ignition, it would take 1.6 times longer for hydrogen to exceed its upper flammability limit of 75% in air and become "safe", than it would take for natural gas to exceed its upper flammability limit of 15% in air. The low value of limiting oxygen index reflects the high value of upper flammability limit for hydrogen. Consequently, the probability of combustion from a random ignition source is greater for hydrogen leakage into a confined space than it is for natural gas. However, because of its higher diffusion and buoyant velocities, hydrogen leaking into an unconfined space would disperse more rapidly. Thus, in an unconfined space a fire hazard would exist more readily with hydrogen than with natural gas or gasoline but would persist in the inverse order .

Susceptibility to Combustion/Detonation: Properties such as high flame velocity, low ignition energy, and small quenching distance indicate a greater hazard potential for hydrogen when compared to other combustible fluids such as gasoline or methane. The wider combustion limits, particularly the lower limit, almost the same as methane's, and lower than many other combustible gases, make it extremely sensitive to combustion. Contributing also to this sensitivity is hydrogen's lower energy of ignition and lower hot-jet ignition temperature compared to both gasoline and methane. This assures ignition in the presence of thermal sources as weak as a spark of static electricity. On the other hand, the high ignition temperature gives hydrogen a favourable comparison. The ignition temperatures of hydrogen-air and hydrogen-oxygen mixtures vary somewhat according to factors of composition, pressure, water vapour content, and initial temperature. At atmospheric pressure, the ignition temperature of either hydrogen-air or hydrogen-oxygen mixtures will not vary greatly from the range 565 to 578 C. The higher burning velocity of the hydrogen-air mixture is an indication of its greater tendency to support the transition from deflagration to detonation in long tunnels or pipes. The data on quenching gap indicates that the dimension required to prevent the propagation of an open flame through hydrogen-air mixture is only 30% of that for methane-air mixture. This property makes the design of flame arresters for hydrogen more complex and difficult, since woven wire screens are unsuitable and sintered metal pads must be used. For hydrogen, the maximum experimental safe gap (MESG), which is the maximum permissible clearance between flanges to assure that an explosion does not propagate from within an enclosure to a flammable mixture surrounding the enclosure, is only 1/15 of that for methane. Therefore, it is more difficult to arrest or confine hydrogen flames and explosions.

Autoignition: The autoignition temperature of hydrogen is 858 K (586 C), compared to 813 K for methane and 501 to 744 K for gasoline. Although the autoignition temperature is higher for hydrogen, its low ignition energy characteristics renders it more susceptible to ignition. The lower hot-air ignition temperature of hydrogen makes it easier to ignite by jets of hot combustion products emitted from an adjacent enclosure, or by adjacent hot surfaces. Above 560 C, hydrogen will combust or detonate spontaneously depending on the concentration present. Thus, a leak or escape of hydrogen due to a high pressure containment rupture would most likely be accompanied by autoignition of the released hydrogen and air mixture with an ensuing conflagration lasting until the contents of the ruptured containment are consumed. Considerable experimental data substantiate this statement (1). For the above reason, it is also inadvisable to "crack" compressed hydrogen cylinder valves before connecting to regulator or manifold (contrary to general practice with other compressed gas cylinders), since "self-ignition" of the issuing hydrogen may infrequently occur (7).

At ordinary temperatures and pressures most common gases (e.g., oxygen, nitrogen, carbon dioxide) are cooled by throttled expansion from high to low pressure. Hydrogen is an exception, and is heated under these conditions. This phenomenon is known as the "Reverse Joule-Thomson Effect". However, the increase in temperature is not very large - about 5.5 C. (10 F.) when throttled from 13.9 M Pa (2000 psig) to atmospheric pressure(7).

Fire Damage: Hydrogen's high buoyant and diffusion velocities make it disperse beyond combustible concentrations fairly rapidly. The scene of a hydrogen fire would tend to be hotter than that of a hydrocarbon fire, but a hydrogen fire will last only 1/5 to 1/10 as long as a hydrocarbon fire (for equivalent fuel spillage volumes) (1). It would also not cover as much area due to hydrogen's buoyancy. The high buoyant velocity resulting from hydrogen's low mass also causes burning hydrogen to rise rather than spread laterally as do hydrocarbon liquids and heavier gases.

As mentioned earlier, LH_2 is much more difficult to contain and the volumetric leakage rate of LH_2 is 2.4 to 8.5 (viscous flow) times larger than LNG. The temperature of methane vapour released from a liquid methane spill must increase nearly 56 degrees C before it becomes less dense than air and disperses. In contrast, liquid hydrogen needs an increase of only a few degrees C to achieve buoyancy in air at standard atmospheric conditions. The higher volumetric vaporization rate and burning rate of a spilled LH_2 pool indicate that a hydrogen fire will be of a shorter duration. The maximum radiated thermal energy from the pool-fed fire is estimated to be 276 W/cm^2 for hydrogen and 155 W/cm^2 for methane. Therefore, the scene of a hydrogen fire will be hotter than that of a methane fire.

The main fire damage parameters are thermal radiation, flame engulfment (fireball), smoke inhalation, fire detection and extinguishment. The flame temperature in air for hydrogen is only slightly higher than that for methane. About one fourth of the heat from these hydrogen and methane flames is transferred by radiation. Water vapour in the air tends to absorb some of the radiation, but less so from methane flames than from hydrogen flames. The fireball damage is the direct result of the combustion of materials initiated through contact with or engulfment by flames that are consuming the hydrogen-air mixture.

Fire Detection: As mentioned above, fire detection is also a safety problem with hydrogen. Hydrogen burns in air cleanly with a pale blue flame and in daylight conditions the flame is virtually invisible. Impurities or moisture in the air make it somewhat more visible and smaller fires can be spotted at night, but usually a heat shimmer is the only visible indication of serious hazard. Hydrogen's flame emissivity, the amount of heat radiated while burning, is low in air and reduces the heat transferred by radiation and thus reduces secondary ignition and burn damage.

To summarize, hydrogen possesses many unique qualities as a combustible substance. In general, it is sensitive to combustion but disperses beyond combustible concentrations relatively quickly. Its flames are clean-burning, nearly invisible and will burn in a vertical flow rather than spreading laterally. Special precautions should be taken regarding its sensitivity to spark ignition and its detection difficulties.

2.3.3 Detonation

The high diffusion and buoyant velocities and the low mass of hydrogen make it nearly impossible to reach explosive concentrations in an open environment. In a closed environment, however, hydrogen's wider detonability range and low ignition energy make it more explosive than methane and gasoline and increase the probability of a high order explosion. Hydrogen's ignition temperature of 560°C mentioned above, is higher than for other gases and mitigates to some extent the danger of explosion but the low ignition energy must be weighted heavily in precautionary measures.

From the data in Appendix A, it is seen that compared to methane and gasoline, hydrogen is a more explosive fuel on a mass basis and a less potent one on a volume basis. The volumetric explosive potential of liquid hydrogen is approximately 1/3 and 1/6 that of liquid methane and liquid gasoline respectively. In gaseous form, hydrogen's explosive energy is approximately 1/3 and 1/20 that of gaseous methane and gasoline vapour respectively.

The same combustion parameters that influence fire hazards also influence the explosive hazards. The flame front of hydrogen, due to its faster-burning property, has a tendency to accelerate in long enclosures. The experimentally observed detonation induction distance in NTP air (the distance required for a deflagration to transit to detonation) is L/D= 100, for hydrogen, i.e., it is quite certain that,for L/D > 100, hydrogen-air mixtures will detonate in the presence of an ignition source. No such data exist for the slower-burning methane-air mixtures, but it is believed that methane-air mixtures will transit from deflagration to detonation if the pipe is long enough and the diameter is large enough. Overpressures due to deflagrations in open air are usually considered negligible. The overpressure and shrapnel hazards associated with ordinary enclosures (L/D < 30) are about the same for hydrogen-air and methane-air; in long tunnels, etc., hydrogen is a greater explosion threat.

Explosive Damage: Explosions that create overpressures and shrapnel are usually expressed as the theoretical equivalent quantity of TNT. The explosive potential per kJ of stored heating value (based on high heat of combustion) is 0.17 (g TNT)/kJ for hydrogen and 0.19 (g TNT)/kJ for methane. Thus, for equivalent energy storage, hydrogen has a slightly lower theoretical explosive potential. Also, as mentioned earlier, hydrogen is more potent on a mass basis, but less so on a volumetric basis. It must be emphasized that only a fraction of this theoretical explosive yield can be realized in an actual open-air mishap because it is virtually impossible to spill or release a large quantity of fuel and have all of it mixed in proper proportions with air prior to ignition. The meagre experimental data available makes it impossible to accurately assess the probable explosive yield attributable to accidental release and ignition of hydrogen and methane. The "energy of explosion" values listed in Appendix A should be considered theoretical maximums, and yield factors of ten percent are considered reasonable for fuel-air explosions.

Various fireball and fire radiation and explosion overpressure criteria, specifically developed for hydrogen, are shown in Figures 3.3-1 and 3.3-2. These are believed to provide conservative criteria for methane (and gasoline). These figures are based on potential fire and explosion hazards in unbarricaded storage and experimental areas and are not indicative of industrial storage standards. Industrial hydrogen storage standards for hydrogen shown in Figure 3.3-3 are much less stringent.

In summary, then, there are three points of note concerning the detonability of hydrogen. First, it is virtually impossible for hydrogen to reach explosive concentrations in an unconfined environment. Second, when the concentrations of hydrogen in the air reach explosive concentrations the mixture can be easily ignited by an energy source as small as a spark of static electricity, other ignition sources or by autoignition. Ventilation in confined areas, and especially under ceilings where escaped gas will gather, is an essential safety precaution to avert the consequences of explosion or combustion.

2.3.4 Reaction with Oxidants. Halogens and Metals

From a chemical standpoint, hydrogen is fundamentally a reducing agent. It reacts violently with oxidizing agents and halogens - fluorine, chlorine, bromine and iodine. The reactivity decreases from flourine to iodine. The reactions occur explosively, particularly those involving fluorine and chlorine and special care must be taken with hydrogen in these cases. Many accidents resulting from hydrogen and chlorine explosions have been documented. The potential hazards are fire and explosions.

Hydrogen has varying degrees of reactivity with metals. It will form metal hydrides with alkali, alkaline earth and most rare earth metals. In actual fact what occurs is not a chemical reaction but the absorption and bonding of hydrogen to the surface. Absorbed hydrogen subsequently diffuses into the bulk of the metal. The exothermic heat of absorption and endothermic heat of desorption can be compared to heats of reaction. Hydrogen does have a physically debilitating effect on crystalline metals.

2.3.5 Metal Embrittlement

Hydrogen atoms which diffuse directly into the interstices of a metal may disrupt the structure and thus affect the physical properties of the metal or alloy. Some types of steel are particularly susceptible to this phenomenon and blistering, cracking or "hydrogen embrittlement" may occur.

When the metal is used for hydrogen containment, the subsequent weakening or fracture of the metal or alloy can lead to explosion hazards from hydrogen leaks.

The term "hydrogen embrittlement" is not well-defined; it is used to describe a variety of effects of hydrogen on the physical and mechanical properties of metals. The mechanisms that cause hydrogen embrittlement effects also are not well-defined. Factors known to influence the rate and severity of hydrogen embrittlement include internal hydrogen concentration, external hydrogen pressure, temperature, hydrogen purity, type of impurity, stress level, stress rate, metal composition, metal tensile strength, grain size, microstructure, and heat treatment history.

Because the mechanism of hydrogen embrittlement often is not well understood, most studies of hydrogen embrittlement describe effects rather than causes. Embrittlement effects can be divided into a number of different categories; different studies often describe the same embrittlement effects in different terms. Based on the nomenclature set forth by a study performed by Battelle Laboratories, seven types of hydrogen embrittlement effects are described below (5) :-

- Opening of the lattice
- Shatter cracks, flakes, and fisheyes
- Hydrogen chemical attack
- Blistering
- Loss of ductility
- Hydrogen stress cracking
- Hydrogen environment embrittlement

The first six types of hydrogen embrittlement effects involve internal (dissolved) hydrogen. The last type of embrittlement effect (hydrogen environment embrittlement) is the result of hydrogen adsorbed on the surface of metal. A detailed description of the seven embrittlement effects follows.

1. Opening of the Lattice: Metal exposed to very high-pressure hydrogen can become filled with small cracks and fissures. In extreme cases, the metal may become permeable to both liquids and gases. The mechanism for this embrittlement effect is not well understood. However, this type of embrittlement has not been observed at hydrogen pressures below 30,000 psi.

2. Shatter Cracks, Flakes, and Fisheyes: Shatter cracks, flakes, and fisheyes can occur during the manufacture of metals. The mechanism for this hydrogen effect involves the trapping of molecular hydrogen in the metal lattice during cooling.

3. Hydrogen Chemical Attack: The effect of hydrogen chemical attack on metals is the development of fissures, resulting in a loss of both strength and ductility. The mechanism for this embrittlement effect is understood. Hydrogen reacts with carbon in the metal to form methane gas. The methane molecule is too large to diffuse through the metal structure and therefore becomes trapped in voids. Sufficient pressure can be generated by trapped methane gas to cause fissures. The following conditions and physical properties are known to affect the rate and/or severity of hydrogen chemical attack:

   - High hydrogen partial pressures favour hydrogen chemical attack.

   - The rate of hydrogen attack on metals increases as temperature increases.

   - Both the rate and severity of hydrogen chemical attack are influenced directly by the carbon content of the steel. In general, both the rate and severity increase as the carbon content of the steel increases.

   - The effect of hydrogen chemical attack on metals increases as the grain size of the metal increases.

   - The temperature history of the metal affects hydrogen chemical attack. In general, cold-working of metals increases their susceptibility to hydrogen chemical attack.

- The presence of some impurities in hydrogen enhances hydrogen chemical attack. Specifically moisture, hydrogen sulfide, and carbon monoxide increase the rate of hydrogen chemical attack.

- Various alloying elements in steels reduce chemical attack of hydrogen on carbon by forming very stable carbides. The elements commonly used to decrease hydrogen chemical attack are thorium, zirconium, tantalum, neodymium, titanium, chromium, vanadium, tungsten, and molybdenum.

These guidelines are generally presented in graphical form (Nelson charts) as plots of temperature versus hydrogen partial pressures. Figure 2.3.1 is a typical Nelson chart showing safe design conditions for plain carbon steel and carbon steel alloyed with molybdenum. The areas below and to the left of the lines on the temperature versus partial pressure curves for the various metal compositions are considered safe zones. As indicated in Figure 2.3.1, even plain carbon steel exposed to temperatures below $500^{o}F$ is capable of withstanding very high hydrogen pressures (greater than 1000 psi).

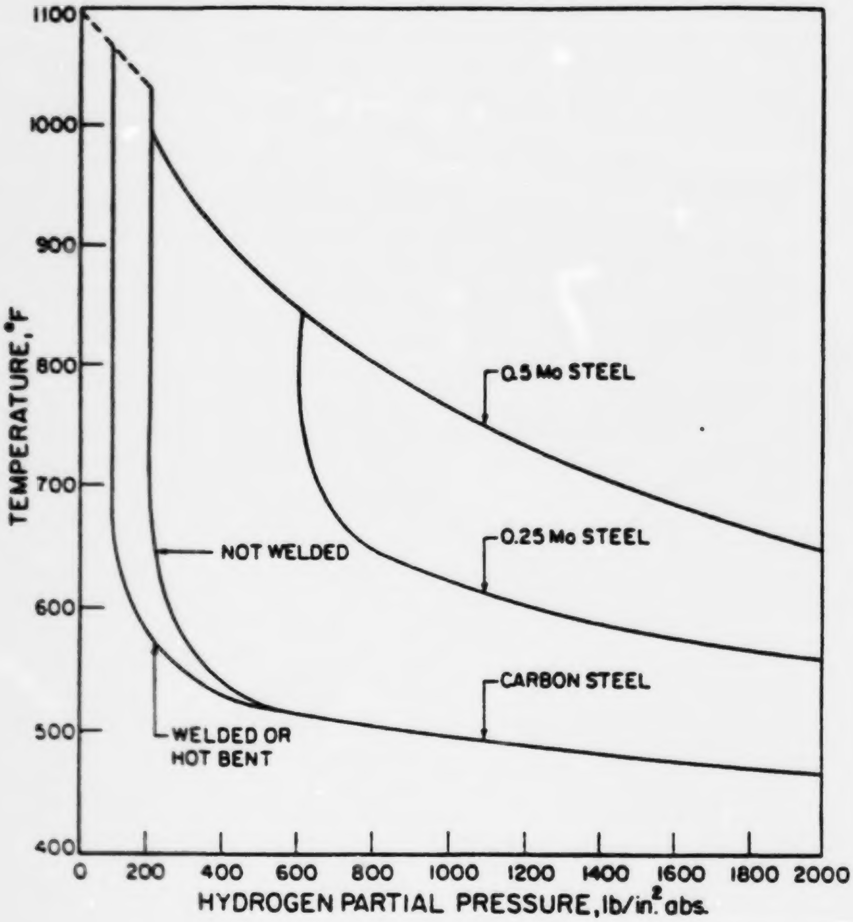


Figure 2.3.1 Nelson Chart of Safe Design Conditions for Plain Carbon Steel and Carbon Steel alloyed with Molybdenum (5)

4. Blistering: Blistering is another hydrogen embrittlement effect whose mechanism is fairly well-understood. Atomic hydrogen diffuses quite rapidly through most metal structures. Molecular hydrogen, on the other hand, does not diffuse and can become trapped in metal structures. In blistering, atomic hydrogen diffuses through a void or defect in the metal structure, recombines at that void to form molecular hydrogen, and cannot diffuse from that void. In such cases, internal pressure in voids due to trapped molecular hydrogen builds up to many times the environmental partial pressure of hydrogen and results in mechanical rupture. The following factors are known to increase the blistering of metals exposed to hydrogen environments:

- Internal imperfections in the metal (laminations, slag inclusions, inclusion stringers) provide sites for the recombination of atomic to molecular hydrogen and increase blistering in metals.
- Corrosion of the metal surface and some surface poisons (such as hydrogen sulfide) increase the concentration of atomic hydrogen at the surface of the metal and therefore increase the internal concentration of atomic hydrogen in metal.
- Reducing metal temperatures quickly favours the formation of molecular hydrogen and results in increased blistering effects.

Blistering may present a problem for some hydrogen applications. This potential problem can be controlled by obtaining high-quality metal (as free of defects as possible), by monitoring and minimizing surface corrosion, and by carefully controlling temperature cycling.

5. Loss of Ductility: In the presence of high internal atomic hydrogen concentrations, some metals (especially high-strength steels) exhibit reduced values of tensile elongation, area in tensile tests, and fracture stress. In severe cases, metal may no longer be capable of resisting fracture in regions of high stress near notches and changes in section size. The mechanism for loss of ductility is not well understood. The effect described as loss of ductility may indeed be a combination of other effects of hydrogen embrittlement. The following factors are known to increase loss of ductility in metals:

ductility may indeed be a combination of other effects of hydrogen embrittlement. The following factors are known to increase loss of ductility in metals:

- Steel tensile strength affects the degree to which ductility losses occur. In general, the higher the yield strength of the material used, the higher its loss of ductility in hydrogen environments.
- Losses of ductility are especially severe in areas that include imperfections and inclusions. The presence of notches also leads to increased ductility losses.
- High internal concentrations of atomic hydrogen (and therefore high external hydrogen pressure) increase ductility losses.
- The hardness of the material of construction also is a factor. Hard spots, especially near welds, are especially susceptible to ductility losses.
- Losses of ductility are most severe at intermediate temperatures (approximately room temperature) and are less severe above and below room temperature.
- The rate of strain exerted on a metal also affects the severity of ductility losses in hydrogen service. Ductility losses are most severe at low rates of strain.
- Cold working of metal increases its susceptibility to loss of ductility in hydrogen service.

Therefore, the design of hydrogen facilities should include use of low-tensile-strength steels wherever possible, proper annealing and welding procedures, and the avoidance of notches, rapid temperature changes, and temperature excursions above or below ambient temperature wherever possible.

6. Hydrogen Stress-Cracking: Hydrogen stress-cracking is an embrittlement effect in which cracks initiate and grow in high-strength steels subjected to stress in the presence of diffusing atomic hydrogen.

The mechanism for this embrittlement is not well understood, but the following experimentally determined conditions are necessary for hydrogen stress-cracking :

a) The metal must have a tensile yield strength above approximately 110,000 psi.

b) The steel must be subjected to a minimum sustained tensile stress. That minimum value of stress depends upon the strength of the steel and its hydrogen content.

c) The steel must contain atomic hydrogen moving through the lattice as a result of concentration of stress gradients.

Factors that increase hydrogen stress-cracking include the following:

- Hydrogen stress-cracking is most severe in steels with high yield strengths.
- Hydrogen stress-cracking is most severe at welds and hard spots.
- The level and rate of stress applied to steel affect hydrogen stress-cracking. In general, a high rate of stress decreases the transport rate of atomic hydrogen through the metal lattice.
- Cyclic stress loadings make a metal more susceptible to hydrogen stress-cracking.
- The presence of hydrogen sulfide and carbon dioxide appears to increase hydrogen stress-cracking of metals.

Hydrogen stress-cracking can be made less severe by adding small amounts of carbon monoxide, water vapour, or oxygen to hydrogen; oxygen, in particular, in very small concentrations has shown the ability to almost completely eliminate hydrogen stress-cracking. Some researchers have determined that alloying steels with some metals can reduce hydrogen stress-cracking, but this observed phenomenon is not well defined at this time.

7. Hydrogen Environment Embrittlement: Hydrogen environment embrittlement is a surface phenomenon in which severe cracks initiate at the metal surface. The mechanism for this embrittlement is not well understood, but two conditions have been experimentally determined to be necessary for this type of hydrogen embrittlement:

   1) The metal must be exposed to an external hydrogen environment. Hydrogen environment embrittlement is not affected by internal, atomic hydrogen.

   2) The metal exposed to an external hydrogen environment also must be plastically deformed.

   The effects of hydrogen environment embrittlement are reversible and do not depend on internal hydrogen concentration. Hydrogen environment embrittlement depends on hydrogen pressure to a limited extent. However, increasing hydrogen pressure by small amounts does not severely increase the rate of hydrogen environment embrittlement. Hydrogen environment embrittlement is much worse in the presence of notches, defects, or changes in section size. There are little data available in the literature on the temperature dependence of this hydrogen embrittlement effect.

   The presence of small amounts of oxygen almost completely eliminates hydrogen environment embrittlement, even in metals that have been severely deformed. Oxygen in concentrations as low as 1 ppm causes a small reduction in the hydrogen environment embrittlement. Oxygen in concentrations of 1% by volume completely eliminates hydrogen environment embrittlement in deformed metals.

   In summary, it is clear that although there is substantial information available to avoid metal embrittlement, further research is required to better understand the exact mechanisms involved in hydrogen embrittlement. The degree of embrittlement is believed to depend upon such parameters as the type of alloy, the operating stress levels, impurities in the hydrogen and probably others not yet recognized. Almost all of the observed hydrogen embrittlement has involved pure hydrogen. Failures resulting from embrittlement have usually been associated with welds rather than the base metal. Small amounts of oxygen, carbon monoxide and other gases are effective in inhibiting hydrogen environment embrittlement. Such impurities may be quite acceptable for almost all energy or industrial uses of hydrogen.

2.3.6 Asphyxiation

Hydrogen is non-toxic, but it can act as a simple asphyxiant by displacing the oxygen in the air. Unconsciousness from inhaling air which contains a sufficiently large concentration of hydrogen can occur without any warning symptoms such as dizziness. Still lower concentrations than those which could lead to unconciousness would be flammable.

Hydrogen is a clean-burning fuel. The by-products of hydrogen combustion in air, nitrogen and water vapour, are not foreign to the lungs, as are the sooty by-products of hydrocarbon or other chemical fires. This removes the danger of intoxication due to inhalation of by-product fumes. The lungs, however, can be damaged by inhalation of the super-heated vapours. As with any fire, there is also danger of asphyxiation when concentrations too rich in hydrogen or its combustion by-products are inhaled for a sustained period of time.

2.3.7 Cryogenic Hazards

The five properties of concern to safety in handling liquid hydrogen (LH_2) are listed in Table 2.3. The cryogenic hazards associated with the storage and handling of liquid hydrogen are discussed below.

Excessive Pressure Build-up within LH2 Containment: As with any cryogen, the large volume ratio between liquid cryogen and room temperature gas (or conversely, the large pressure necessary to maintain liquid density at ambient temperature) gives rise to a mechanism for a large pressure build-up in closed containers. The low normal boiling point (20.3 K for equilibrium LH_2) implies the existence of a large thermal driving force attempting to force heat from the surroundings into the LH_2. Since there is no perfect insulation, this heat input can only be minimized (or avoided by an additional refrigeration process). In addition, the low volume latent heat of vaporization indicates that larger quantities of stored liquid will be evaporated per unit of energy input. It is essential that the boil-off gas must be allowed to vent (usually to the atmosphere). If the resulting gas is not vented, the pressure will rise until either a relief valve opens, an equilibrium pressure is reached, or the vessel ruptures. The pressure rise rate of nonvented LH_2 dewars has been studied. For cases where thermal equilibrium is established within the dewar, the rate of pressure rise can be estimated by calculation using the first law of thermodynamics. However, LH_2 dewars will usually stratify thermally, thus giving rise to pressure rise rates up to an order of magnitude higher than those calculated with the assumptions of complete thermal mixing.

Some smaller dewars have thermal radiation shields that are cooled by the venting vapors, thus gaining a lower boil-off loss by utilizing some of the refrigeration available in the cold venting vapour. For such a dewar, the stopping of venting for any reason will result in an increased heat leak (by up to, perhaps, a factor of 10) and consequent faster pressure rise.

Air Condensation: LH2 is sufficiently cold that, if any air is allowed to enter the storage vessel or its vent system, the air (in addition to any moisture it contains) will condense to a solid and exert essentially zero vapour pressure. This is a potential hazard for several reasons. First, it forms a combustible mixture. Also, the air so condensed is very difficult to detect so that a considerable amount of accumulation can result. In addition, a large fraction of this air can condense within the storage vessel vent tube where the temperature is at the freezing point of air. A sufficient accumulation at this point can plug the vent tube, thus starting a pressure build-up which eventually can result in a catastrophic failure of the storage vessel. This type of accident has occurred.

Air condensation can also be dangerous when it occurs externally to the LH_2 system. Cold hydrogen gas or LH_2 being vented through uninsulated pipes will usually condense liquid air on the outside of the pipes. If this air is allowed to drip onto a combustible surface, such as asphalt, an explosive mixture can result. For this reason, LH_2 unloading or transfer areas are usually paved with concrete instead of asphalt. The dripping liquid air can also be hazardous if allowed to fall onto other equipment that can be disabled by being cooled too much, too unequally, or too rapidly. This phenomenon has cracked deck plates on LH_2 transport barges and even the outer shell (carbon steel vacuum jacket) of a vessel from which cold hydrogen was being discharged.

Excessive Thermal Stresses: It should be pointed out that, even without cooling from LH_2 being vented, there frequently exist large temperature gradients within equipment handling LH_2, and care must be taken to avoid excessive thermal stresses as well as the inadvertent cooling of any equipment which could be damaged by cooling. This could arise either from cold embrittlement (a large loss of ductility as temperature is lowered) or thermal contraction in excess of that allowed for in the design of the equipment.

The piping system and storage vessels in LH_2 systems are obvious places where temperature gradients must be considered in both the design and the planning of operating procedures. Temperature gradients will always exist in the cool-down to operating temperature, and frequently the residual temperature gradient remaining after reaching thermal equilibrium can also give rise to prohibitive stresses.

Cold Embrittlement: Cold embrittlement of metals is a well-known hazard associated with cryogenic fluids such as liquid hydrogen and cold hydrogen gas. The handling of hydrogen gas does not present any low temperature problems, as a rule. However, if hydrogen gas stored at high pressure (say, 100 atm) is allowed to vent very rapidly, the temperature of the gas discharged will become colder as the venting proceeds over a period of time. This might not be normally expected since the Joule-Thomson expansion across the vent valve is at a temperature above the inversion temperature, and the gas actually warms a few degrees as it expands by this process. However, the gas still in the tank is expanding adiabatically (since the thick tank wall does not permit a rapid enough influx of heat to maintain the temperature). The latter effect can cool the remaining gas tens of degrees, with the result that the exhaust stream constantly drops in temperature. Cold embrittlement of the vessels, which are not intended for use at low temperatures, is a possible hazard to be considered under these conditions. Stainless steel inserts have been installed in the discharge tube in places where the rapid heat transfer to the flowing gas could cool the vessel walls excessively (2).

Cold Injury to Humans: Liquid hydrogen can also cause cold injury to humans if proper precautions are not taken. Exposure to liquid hydrogen or uninsulated liquid hydrogen lines can result in tissue damage from frostbite. Liquid hydrogen which boils quite violently and vaporizes rapidly on contact with skin, will float on the skin over a thin vapour film. Thus, if contact lasts only for a few seconds, the probability of extensive frostbite is low.

In summary, the low temperatures encountered in cryogenic hydrogen systems (typically down to 20K [-425 F]) can cause hazards in other equipment and in structural members. One must consider the potential hazards arising from changes in physical properties. In addition to the obvious necessity of allowing for thermal contraction, there is also the possibility of embrittlement due to the low temperature. Contact with frosted lines, condensate that may be dripping from cold lines or vent stacks, vaporizer fins, and vapour leaks could cause frostbite and should be avoided. Insulation, equipment integrity, escape detection and secondary precautionary measures are important to maintaining a safe industrial facility for cryogenic hydrogen.

TABLE 2.3 CRYOGENIC PROPERTIES RELATED TO SAFETY

Electrical resistivity of LH2 (Ohm-cm)	$\sim 4.6\times10^{19}$
Volume ratio (gas at 1 atm and 300K to LH2)	860
Pressure to maintain LH2 density in gas at 300 K (atm)	~ 2000
Normal boiling temperature of LH2 (K)	20.3
Volume latent heat of vaporization (J/l)	31,700

3. RISK AVERSION METHODS

The above hazards and how to avoid them must be given prime consideration in all phases of any hydrogen operation, including system design, construction, checkout, operation, maintenance and modification. As mentioned earlier, a thorough knowledge and understanding of the hazardous properties of hydrogen and their relation to potential hazards and hazardous environments is an essential prerequisite in the safe design and operation of hydrogen systems. The system and equipment must be designed and built so that they allow for safe operation. Operations should be according to preconceived plans, which include standard operating procedures as well as contingency procedures. These procedures should be written, and the documents should be reviewed regularly. The avoidance of hazards must always be considered, and the system should be operated only as planned, which includes staying within anticipated pressure, flow rate and temperature limits. Operator training should be an on-going practice. A continuing safety program should include experiments to learn more about the safe operation of the system and to demonstrate these principles to others.

Certain general guidelines and codes of good practice for avoiding or minimizing hazards have been developed by the scientific and industrial communities, and government organizations, based on the understanding of the hazardous and unique properties of hydrogen and from the industrial experiences and practices in the production, storage and handling of gaseous and liquid hydrogen. Various analytical techniques have been developed and successfully applied in industrial systems to identify, analyse and assess potential hazards and to propose appropriate risk aversion methods. The established hydrogen safety practices as well as the available analytical techniques for identifying and assessing hazards are outlined in this section.

The general industrial practices and guidelines for risk aversion in hydrogen systems are:

- Compliance with Codes, Standards and Guidelines
- Quantity Limitation for Indoor Storage
- Location and Separation of Process and Storage Equipment
- Control of Hydrogen Accumulation within Enclosures
- Exclusion of Air
- Elimination of Ignition Sources
- Leakage Detection and Control
- LH2 Spill Containment
- Instrumentation
- Safety Reliefs
- Safe Venting and Disposal
- Selection of Proper Materials of Construction
- Cryogenic Precautions
- Fire Detection, Control and Extinguishment
- Hazard Identification and Assessment

3.1 COMPLIANCE WITH CODES, STANDARDS AND GUIDELINES

Personnel safety requires strict adherence to industrially accepted standards and guidelines and compliance with existing regulatory codes. The word "codes" refers to regulations (mandatory) and standards (nonmandatory or mandatory). Codes of regulations are mandatory and enforceable, but codes of standards are nonmandatory unless they are specified in the regulatory codes of . regulatory authorities. Various interdisciplinary committees, with industrial, government and university representatives, have published guidelines for safe procedures to be followed throughout the various phases of producing and using hydrogen. Some of these publications have been accepted industry-wide as national standards and these standards are mandatory and enforceable when they are adopted by regulatory bodies, state and city governments, etc. Insurance companies usually adopt or specify existing standards, practices and procedures as a condition of insurability for industrial organizations. Examples of nonmandatory standards that may be adopted by regulatory bodies are those issued by the ASME, ANSI, ISA, NFPA, UL, etc.

Existing codes and regulations specifically for hydrogen operations are mostly concerned with its transportation. Other phases are covered by more general regulations, and a recent and excellent listing is given by Hord (1,8). The various codes, standards and guidelines applicable to the production, storage and handling of hydrogen are summarized in Section 4.

3.2 QUANTITY LIMITATION

Limiting the quantity of hydrogen stored and handled indoors is considered essential in minimizing the extent of hydrogen escape through accidental leakage and preventing the accumulation of hazardous hydrogen - air mixtures. The extent of fire and explosion damage to personnel and property can also be minimized by limiting the quantity of gaseous and liquid hydrogen stored and handled indoors. The national, provincial and municipal building and fire codes usually specify the maximum allowable quantity of flammable liquids and gases for indoor storage. The two National Fire Protection Association (NFPA) Standards, i.e., NFPA 50A for Gaseous Hydrogen Systems at Consumer Sites and NFPA 50B for Liquefied Hydrogen systems at consumer sites, specify the maximum allowable quantity of hydrogen stored and handled in small scale, at consumer sites.

3.3 LOCATION AND SEPARATION OF EQUIPMENT

In establishing the safe distance required for the large scale storage of hydrogen, either from hydrogen storage vessels to inhabited buildings or between hydrogen storage vessels , recognition should be given to the nature of the potential hazard that the hydrogen containing vessels present to the surroundings as well as the hazard that the surrounding environment presents to the hydrogen containing vessels. Facilities which handle hydrogen should be kept free from secondary hazard, such as other combustible materials. Items of equipment associated with the greatest quantities of hydrogen, such as the storage tanks and the liquefaction unit LH_2 cold boxes, should be located at a considerable distance away from heavy traffic areas. Adequate space must be provided around each item of equipment and egress routes must be provided in case of fire or other emergency.

The extent of hazard resulting from a leakage or spill is dependent not only on its proximity to storage tanks, buildings, concentrations of people, etc., but also on the size of the leakage or spill and whether the hydrogen ignites. Obviously, the greater the quantity that is leaked or spilled, the greater the hazard upon ignition, and the greater should be the clearance. Due to its very low ignition energy and very wide combustibility limits in air, it must be assumed that fire accompanying a hydrogen leakage or spill will be the rule rather than the exception. On the other hand, an unconfined hydrogen-air mixture will ignite in a deflagration, not a detonation. This means that blast damage will be minimal. The resulting hydrogen flame is invisible and has a temperature of about 2317 K (3710° F). Despite the high temperature, the flame has a low emissivity and radiation effects on nearby equipment will not be as severe and clearances need not be as great. Also because of its high volatility, an LH_2 spill will vaporize rapidly and the resulting fire will not be as long in duration as an equal spill of hydrocarbon liquid.

Quantity-Distance Requirements: The following National Fire Protection Association Standards contain specifications for the location and separation of process and storage equipment containing hydrogen:

- NFPA No. 50A for Gaseous Hydrogen Systems at Consumer Sites;
- NFPA No. 50B for Liquefied Hydrogen Systems at Consumer Sites.

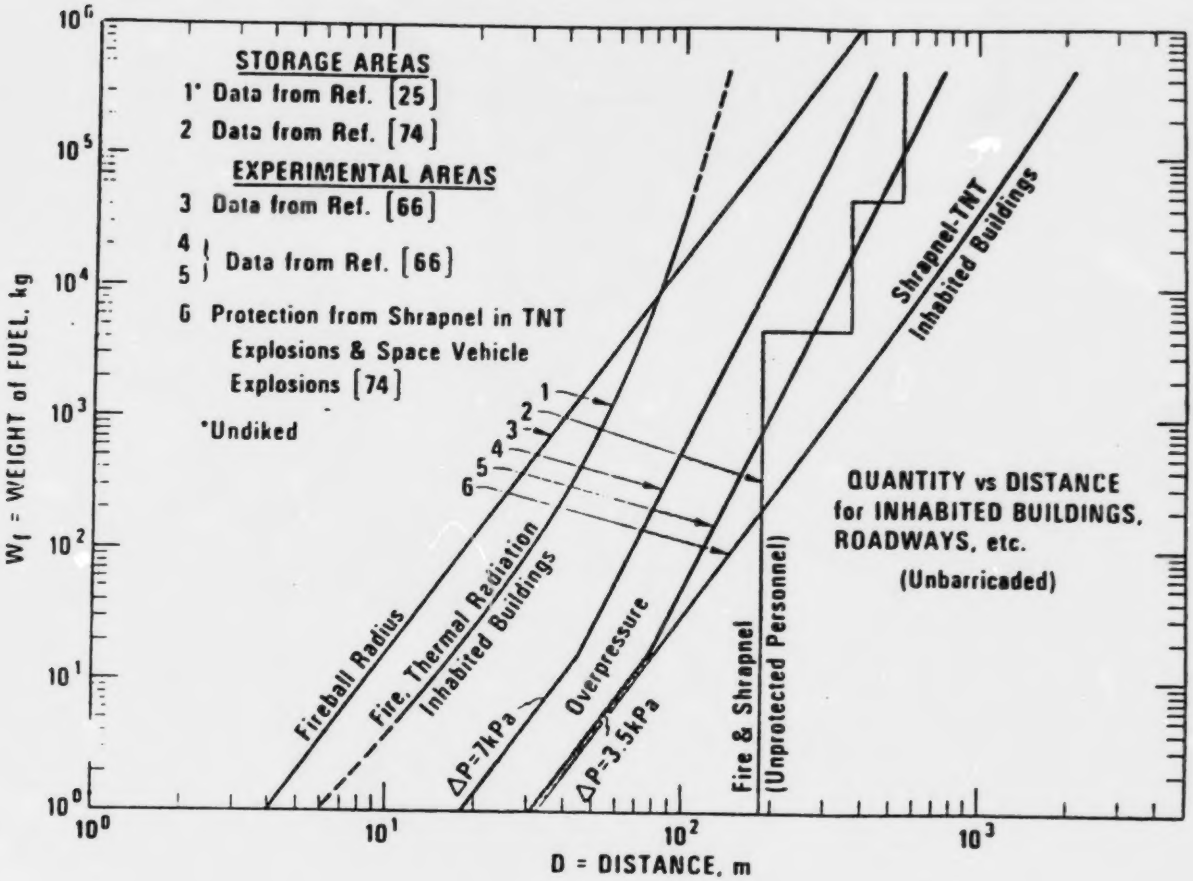
These two standards are intended for small scale usage at consumer sites and both specifically exempt manufacturing plants or other establishments operated by the hydrogen supplier for the purpose of storing hydrogen and filling operations.

Several different governmental organizations have published guidelines for distances of separation for the storage of liquid hydrogen. These distances, which are a function of the total quantity stored, are given as either the distance from the unbarricaded storage to concentrations of people (i.e. inhabited buildings - Figure 3.3-1), or as the distances between adjacent dewars (Figure 3.3-2). The overpressure band on Figure 3.3-1 corresponds to breakage of ordinary window glass (3.5 to 7 kPa) and the overpressure band on Figure 3.3-2 relates to the estimated external pressure capability of liquid hydrogen storage dewars. The derivation and use of data shown on these figures (safe unbarricaded distances) are fully discussed in a summary document (9) treating the explosive hazards of hydrogen. Unbarricaded distances required for the protection of personnel in inhabited buildings that are exposed to shrapnel from TNT explosions are indicated by Curve 6 on Figure 3.3-1.

Figure 3.3-3 provides a ready comparison of industrially accepted fuel storage standards for liquid hydrogen, LNG and gasoline. By comparing Curves 1 and 4 on Figure 3.3-3 with the data given on Figures 3.3-1 and 3.3-2, it is seen that the industrial quantity - distance standards for hydrogen are less demanding than those suggested for experimental areas. Experience indicates that the number of accidents occurring to vessels being used in an experiment greatly exceeds that for vessels being used exclusively for storage. A comparison of Curves 1 and 2, and 4 and 5 on Figure 3.3-3 also indicates that the industrial storage standards are more restrictive for LH_2 than for LNG. The quantity-distance requirements for liquid hydrogen (proposed by the Bureau of Mines) and for LNG (Canadian Standards Association Standard Z276-M1981) are compared in Tables 3.3-1 and 3.3-2. The proposed distances for LH_2 are based on 1% moisture in the atmosphere and exclude shock-sensitive materials; they agree well with Curve A of Figures 3.3-1 and 3.3-2.

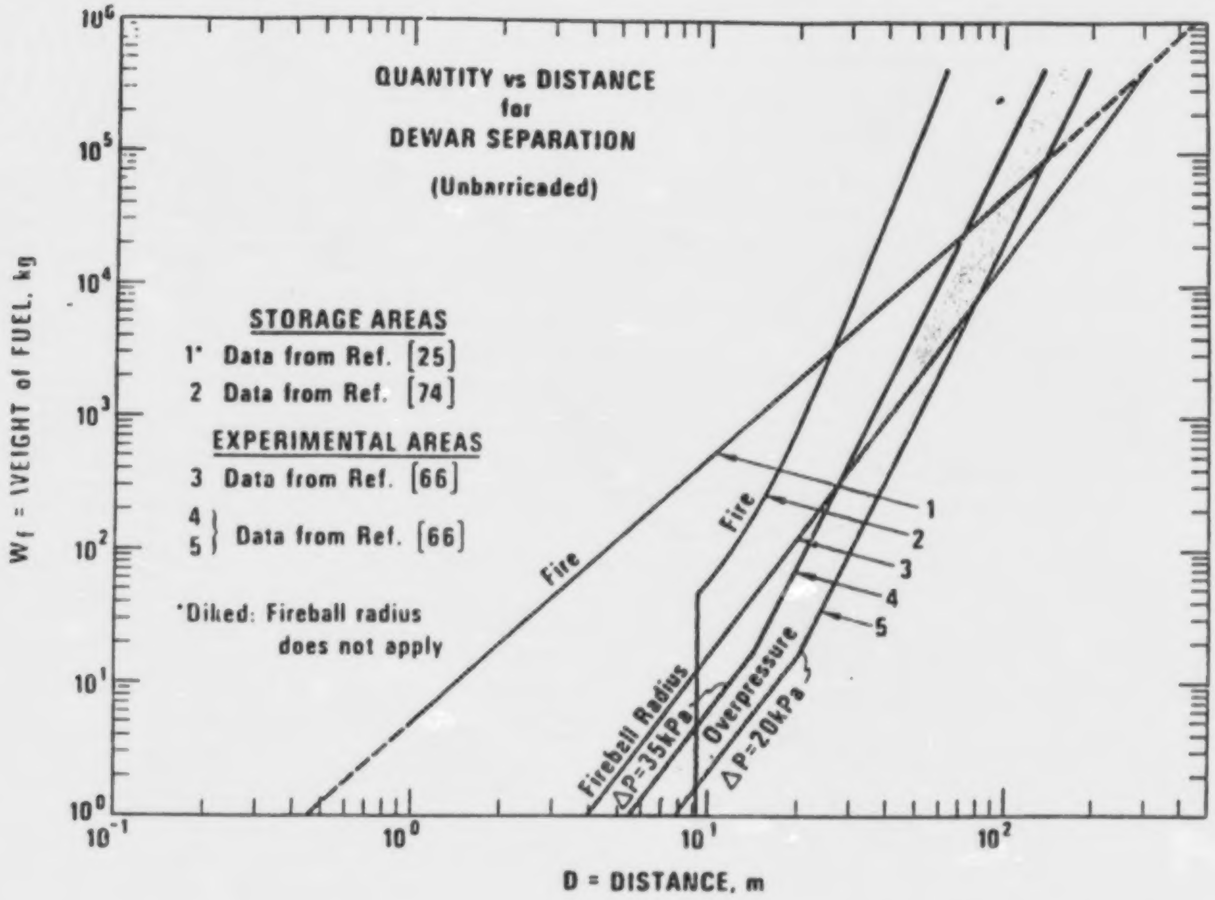
A single series of documents (10) offers a comprehensive treatment of overpressure, impulse, fireballs, shrapnel, barricades, structural response and physiological effects, as they relate to propellant explosions. These documents are believed to be applicable to fuel-air explosions where TNT equivalent is properly estimated. A thorough compilation, analysis and correlation of available fragmentation data for exploding liquid propellant tanks, and gas storage vessels, has been published by NASA (11,12). The review article by Strehlow and Baker (35) summarizes the state-of-the-art concerning characterization and evaluation of accidental explosions.

In summary, considerations which affect the quantity distance relationship for safe hydrogen storage are the quantity stored, possible fireball size, flame radiation, shrapnel damage, and overpressure. The intensity vs. distance of radiation from a hydrogen flame is strongly dependent upon the amount of water vapour in the air. Also, the uncertainty in actual energy release to be expected makes difficult the evaluation of damage due to shrapnel and overpressure. A number of quantity-distance recommendations have been made by several authorities for the safe storage of hydrogen. The differences in the recommended separation distances illustrate the variation in conservatism of the various authorities that generate the safety criteria and the differences of opinion concerning the magnitude of a credible accident. Obviously, when in doubt, the more conservative criteria should be used.



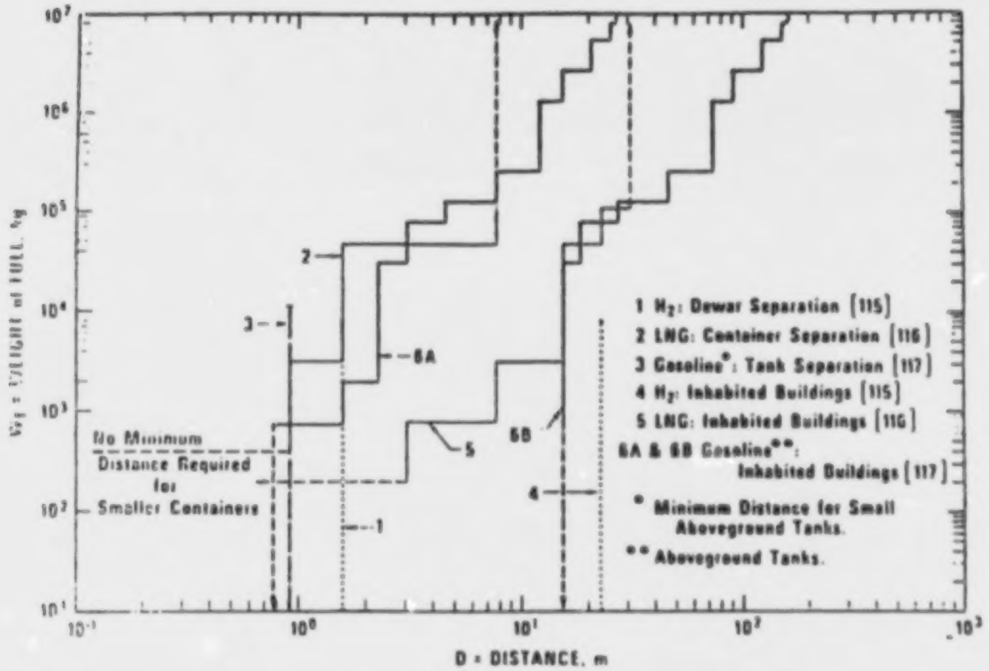
QUANTITY-DISTANCE RELATIONSHIPS FOR THE PROTECTION OF PERSONNEL NEAR LIQUID HYDROGEN STORAGE AND EXPERIMENTAL AREAS (UNBARRICADED)

Figure 3.3-1



QUANTITY-DISTANCE RELATIONSHIPS FOR LIQUID HYDROGEN DEWAR SEPARATION IN STORAGE AND EXPERIMENTAL AREAS (UNBARRICADED)

Figure 3.3-2



INDUSTRIAL STORAGE STANDARDS (QUANTITY-DISTANCE) FOR HYDROGEN, LIQUEFIED NATURAL GAS (LNG) AND GASOLINE

Figure 3.3-3

TABLE 3.3-1 DISTANCE BETWEEN ADJACENT CONTAINERS

LIQUID QUANTITY (kg)	DISTANCE (m)	
	LH_2	LNG
Less than 210	15	None
211 - 420	15	None
421 - 900	15	0.9
901 - 3210	30.5	0.9
3211 - 4537	30.5	1.5
4538 - 9075	45.7	1.5
9076 - 18150	60.96	1.5
18151 - 27225	76.2	1.5
27226 - 45372	91.4	1.5
45373 - 48170	-	1.5
48171 - 111990	-	3
Over 111990	-	*

* 1/4 of sum of diameters of the two adjacent containers, but not less than 7.5 m.

TABLE 3.3-1 DISTANCE FROM CONTAINER TO INHABITED BUILDINGS

LIQUID QUANTITY (kg)	DISTANCE (m)	
	LH_2	LNG
Less than 90	30.5	None
91 - 210	45.7	None
211 - 420	45.7	3
421 - 800	61.0	3
801 - 2269	61.0	7.5
2270 - 3210	76.2	7.5
3211 - 9074	76.2	15
9075 - 18149	91.4	15
18150 - 45372	106.7	15
45373 - 48170	-	15
48171 - 111990	-	22.5
Over 111990	-	*

* 0.7 times the container diameter, but not less than 30.5 m

3.4 CONTROL OF HYDROGEN ACCUMULATION WITHIN ENCLOSURES

It is the preferred procedure to contain all hydrogen within the using system. If small amounts of leakage do occur inside a building, roof vents and sufficiently rapid forced ventilation, where practical, are accepted methods to assure that no explosive mixtures will occur. However, in some cases where very large amounts of hydrogen are involved and the possibility of large leaks exist, it might not be possible to provide adequate ventilation. In these cases, the dilution of the entire room with an adequate quantity of an inert gas, such as nitrogen, is preferred. The oxygen concentration should be monitored and additional inert gas should be introduced until the concentration of oxygen is below 4%. In order for any personnel to enter the room with this procedure, it is necessary that either deinerting takes place or the entering personnel wear self-contained breathing apparatus. For a well-sealed room, 1.7 times the room volume of gaseous nitrogen is required to perform the initial inerting.

3.5 EXCLUSION OF AIR

The basic design concept for any system involving hydrogen consists in exclusion of air from either gaseous or liquid hydrogen systems. This is accomplished by providing a closed system for gaseous or liquid hydrogen with means of venting and evacuation or inert gas purging, and adequate monitoring. To avoid unwanted hydrogen-air mixtures, provision must be made to allow the purging of air from the equipment before admitting the hydrogen. After operation, it is also advisable in most cases to purge the remaining hydrogen from the system. In gaseous systems, helium or nitrogen is commonly used as a purge gas and liquid systems are purged with helium. For equipment with a low length to diameter ratio, such as a spherical dewar, it is usually best to evacuate the vessel to a residual pressure of no more than a few torr, and then backfill with either hydrogen or an inert gas such as nitrogen or helium. If directly backfilling with hydrogen, the evacuation should be to a pressure low enough that there is no chance of creating an explosive mixture at any time during the purging process. One can also pressurize the container to some elevated pressure with an inert gas, and then vent the resulting mixture, repeating this procedure until a sufficient purge has been obtained.

Either of these procedures can take a number of cycles before a satisfactory purge is obtained. For vacuum purging the system must be designed for vacuum conditions.

For equipment with a long length-to-diameter ratio, it is frequently better to use a flow-through purge. An example of this type of equipment is a transfer line or pipe. Care must be taken to avoid dead ends in the piping system, and where they must exist, some of the purge gas must flow out an additional vent at the end of the side branch.

For any purging operation, one should not rely upon calculation of the degree of purge obtained. Rather, samples should be taken from several points of the system and analyzed for residual traces of air.

Except in unusual circumstances, LH_2 should be stored at a pressure above that of the surrounding atmosphere so that any leakage will result in hydrogen escaping rather than air entering the storage dewar. For low boil-off dewars, the vent system should make provision for preventing backflow of air. Also, the velocity within the vent system should be maintained high enough so that appreciable quantities of air cannot enter the dewar by the slow back-diffusion of air through the stagnant boundary layer of hydrogen adjacent to the vent tube wall.

3.6 ELIMINATION OF IGNITION SOURCES

With the use of hydrogen systems, it is always necessary to control ignition sources. This includes the prohibition of smoking, open flames, etc., within specified distances as well as eliminating other potential ignition sources such as sparks from electrical equipment, hot gases and surfaces, and static electricity. Because of its low minimum ignition energy (0.02 mJ), even a weak spark, such as that produced in an electrostatic discharge, is considered to be sufficient to ignite a stoichiometric hydrogen-air mixture. The most likely causes of static electricity are the action of contact and separation of dissimilar materials, solid impurity particles travelling through the piping systems and contact with the human body (10 mJ sparks may be produced in such electrostatic discharge). The extremely high electrical resistivity of LH2 reduces the likelihood of electric charge accumulation in flowing LH2, although the flow of two-phase hydrogen can allow the accumulation of some charge which can persist. In any flow system involving combustible fluids, one cannot afford the assumption that static charges do not exist and must, accordingly, make provision for draining them away. Therefore, every piece of process equipment, every storage tank, and every other system component must be attached to an adequate grounding system. All gasketed pipeline joints must be bridged with an electrically conductive bonding strap. Any piece of equipment which is not normally grounded and which is to be connected to the hydrogen system must first be electrically connected by suitable means. Personnel engaged in making and breaking hydrogen line connections must have provision for grounding themselves such as conductive-sole shoes. The electrical grounding systems must also be periodically inspected and maintained to ensure their integrity. The importance of electrical grounding cannot be overemphasized. Tc compromise on a ground which is less than entirely adequate is to introduce the potential risk of ignition caused by static discharge resulting in a serious fire.

Elimination of ignition sources from other equipment is much more difficult to control. A number of hydrogen systems require the use of many auxiliary electrical and electronic equipment in which it is very difficult to eliminate all of the ignition sources. Electrical equipment in certain applications may have to conform to electrical safety codes and explosion-proof equipment are specified for use in hazardous locations. Explosion-proof equipment is equipment that will contain an ignition within the case. However, due to the small quenching distance for a hydrogen flame, the manufacture of such equipment is difficult. Therefore, if equipment which could become an ignition source must be located within an area where combustible mixtures of hydrogen and air could occur, this equipment is frequently contained within an enclosure which is purged with nitrogen gas in a manner analogous to the room inerting mentioned earlier.

In cases where it is necessary to dispose of hydrogen continuously to the atmosphere (LH_2 storage is such an example), ignition control is not completely possible, since ignition can occur from natural causes, such as electrical storms. A direct lightning strike is not necessary since the corona discharge accompanying lightning striking within hundreds of feet can ignite the venting gas. LH_2 storage systems should be equipped with vent systems that allow for such a fire with no damage resulting.

3.7 LEAKAGE DETECTION AND CONTROL

In any hydrogen system, the hydrogen concentration should be constantly monitored using suitable detectors. Current practice considers 20% of the lower flammability limit (LFL) as hazardous. If the detected gas level reaches a value equal to 50% of the LFL, the gas supply should be stopped and the system should be safely shutdown (36).

A review of the extensive literature on hydrogen handling and safety generated from NASA's and the U.S. Air Force's experiences indicates the extremely cautious and conservative approach to hydrogen, emphasizing leak detection as a major consideration (6, 13, 14, 15). In spite of the unfavourable leakage characteristics, industrial experience has proved that both liquid and gaseous hydrogen can be safely and easily contained.

Leakage Detection: A fairly broad selection of detectors is now commercially available, and more are being developed. Techniques for detection of hydrogen leakage are summarized in two documents (13, 14) and general procedures for leak testing are detailed in the handbook by Marr (14). The most widely used portable and fixed hydrogen detectors are of the catalytic combustion type. Portable ultrasonic detectors are also in use, although background noise could cause some difficulty with this type of detector. A summary of the hydrogen fire- and leak-detection practices, based on a survey of industrial plants and other hydrogen users, is presented in tabular form in Appendix `B' (6, 13).

Leakage Control: The amount of hydrogen which may escape from a leak should be limited by stopping the gas flow (shutting down pumps, compressors, valves, etc.), and by isolating the equipment and lines using shut off valves. For gaseous hydrogen systems, the ring and blind flange design is considered to provide satisfactory isolation. Another solution is the "double block and bleed" in which two valves are placed in series, and the volume between these valves is vented to the atmosphere.

For the isolation of the liquid discharge line of an LH_2 storage dewar, neither of the above methods is satisfactory. For this purpose a so-called "helium block" can be used. Here two liquid shut-off valves are placed in series. After an LH_2 discharge is completed, the line is purged with helium gas at a slightly higher pressure than the LH_2 storage dewar. If a " double block-and-bleed " method were attempted, a small amount of leakage out of the dewar would first destroy any gas block (or trap) which was included in the system to minimize heat leak from the shut-off valve into the dewar. Then the cooling of the valve would increase the leakage as the valve becomes progressively colder. With the helium block, any small amount of leakage will be only of helium gas and into the dewar. A hydrogen system should be made safe under the assumption that any valve in the system can leak at any time.

3.8 LH2 SPILL CONTAINMENT

Another safety precaution necessary in LH_2 storage relates to the containment of accidental LH_2 spillage. Liquefied natural gas (LNG) storage facilities are generally required by law to be provided with impounding structures to contain liquid spills and to prevent fire and radiation hazards to adjacent storage tanks, buildings, roadways, etc. However, such a degree of confinement for LH_2 storage is considered to influence the combustion following a massive tank failure to transit to a more destructive detonation rather than a simple deflagration. LH_2 dewars can be surrounded with low dikes which are only large enough to contain the dewar contents in the case of a major tank rupture. Where the dewar is sufficiently isolated, a preferred alternative is the contouring of the surrounding terrain so that any large quantity of spilled hydrogen would be allowed to flow away to a location where the possible fire would be less destructive. A tentative major finding of the recently completed rapid LH_2 spill experiments, such as those which might occur as a result of a LH_2 storage facility rupture, is that the use of dikes around LH_2 storage facilities would probably enhance prolonged ground-level flammable cloud travel and that it may be preferable to not use dikes and to take advantage of the dispersion mechanisms provided by spill- and vaporization-induced turbulence (17).

3.9 INSTRUMENTATION

As mentioned earlier, hydrogen is colorless, tasteless, and odorless, and it burns with an almost invisible flame. Furthermore, LH_2 is a very volatile liquid, and to cut the heat leak into the system, every effort is made to cut all radiation to it, even visible light radiation. For this reason, in a well-designed and operated system, LH_2 is seldom, if ever, seen. This characteristic of hydrogen makes the operator completely dependent upon the instrumentation for the safe, reliable, and efficient operation of the system.

Therefore, a very important part of any system for handling hydrogen is proper instrumentation which, in general, includes temperature, pressure, flow, liquid level (in the case of LH_2), and hydrogen detection. All of these measurements can have a great significance in the safe operation of the system, and provision for their inclusion should be recognized in the initial system design. Instrumentation should not be an afterthought, but rather should be considered early in the conceptual design of the system. In this way, there will have been provided the necessary sampling ports as well as the hydrogen-monitoring equipment and gas analyzers. Frequently, it is much more expensive and sometimes impossible to add desired temperature measurement points or sample ports once the equipment is built.

The H_2 detection equipment is obviously important, and to obtain the best results from this type of system, it is necessary for the operator to understand both the principle of operation (thermal conductivity or catalytic oxidation) as well as the individual idiosyncrasies of the detectors. The latter includes system response time as well as possible sources of false alarms. Also, it is usually best not to depend upon a single sensor.

3.10 SAFETY RELIEFS

In any system containing either LH_2 or cold hydrogen gas, it is necessary to provide for pressure relief to prevent any unwanted pressure rise when the system finally warms up to ambient temperature. LH_2 storage dewars are usually equipped with a venting system that is designed to provide for normal pressure relief at a preset pressure level backed up by a safety pressure relief valve and finally by a rupture disc. The safety relief valve should be checked periodically and, the rupture disc should be replaced at preset intervals, since it can either suffer from work-hardening (which could raise its relieving pressure) or from fatigue (which could lower its relieving pressure). If dewar pressurization gas must enter the dewar, it frequently is necessary to provide within the dewar a diffuser inlet that prevents the incoming gas form impinging directly upon the liquid surface.

The storage dewar is not the only place where it is necessary to provide for pressure relief. Three other types of spaces also require similar pressure relief:

a. Any section of transfer line or any container where either LH_2 or cold H_2 gas can be isolated between two valves, either intentionally or inadvertently;

b. An internal experimental gas volume which relies on external LH_2 to keep it cold.

Here, the loss of refrigeration could cause unwanted pressure build-up; and finally,

c. The vacuum insulation space which is usually used to surround the cryogenic system.

The cold inner surface of the vacuum space is an excellent cryopump for any air that might leak in. At the LH2 temperature of 20 K, the vapor pressure of N_2 is approximately 10^{-11} torr, and therefore, fairly large quantities of air that could have leaked in over a long period of time would not be detected. Upon removal of the cryogen from the system, its subsequent warm-up could then cause a rapid pressure rise in the vacuum space due to the consequent warming of the trapped air.

3.11 SAFE VENTING AND DISPOSAL

Vent stacks should be provided for the disposal of small quantities of hydrogen gas which may be vented from time to time. Examples include vented gas from safety valves, rupture discs, blowdown valves, etc. The various vent lines leading from such sources should terminate in a vent stack which is sufficiently above all equipment and buildings. The stack and interconnecting piping should be sized to accommodate the maximum flow which must be vented in any conceivable situation. The stack should be located so that prevailing winds do not carry the effluent from the stack to a hazardous area. For disposal of abnormal quantities of hydrogen, simple vent stacks are inadequate to accomplish the job in a safe manner. For venting large quantities of hydrogen in a short time (in excess of several hundred grams per second) disposal is best handled by means of a burnoff system in which the liquid or gas is piped to a distant location and burned in a suitable flare. The installation should include adequate monitoring for flame-out protection and means for purging the line. A check valve arrangement should be provided in the line to prevent back-diffusion of air.

For routine venting of LH_2 storage dewars, the flows are usually small enough that the venting can be directly to the atmosphere with no provision for flaring the vented hydrogen gas. Under normal circumstances, this venting will only amount to about 1 g/sec. In large scale LH2 storage, as a rule, it should be attempted to make each storage dewar for LH_2 independent of the rest of the system. This means that the normal boil-off losses should be vented from a local vent stack completely separate from the rest of the system. In this manner, there is no interaction that could cause a problem in the dewar due to any problem in some other part of the system. In the event of fire when large quantities are being vented, it is not always best to extinguish a fire. If the venting can be stopped, the possibility of hydrogen accumulation may present a greater hazard than the existing fire.

The vent stack can also be equipped with a helium supply. In the event of a stack fire, a slow helium flow can be started, next the hydrogen can be valved off, and the helium allowed to continue to flow until the top of the vent system has cooled sufficiently that no reignition will occur. This will take about 5 minutes. Then the hydrogen venting can be restarted, and finally the helium flow can be stopped.

Another method of disposing of large quantities of hydrogen is by use of a burn pond. With this method, the hydrogen is released by being allowed to bubble up through a pond of water and burn at the surface of the water.

3.12 FIRE DETECTION, CONTROL AND EXTINGUISHMENT

Hydrogen flames are nearly invisible in daylight but their visibility is improved by the presence of moisture and/or impurities in the air. Hydrogen fires are readily visible in the dark or in subdued light and large hydrogen fires are quite detectable in daylight because convective "heat ripples" are visible in the air at near-range distances and thermal radiation heats the skin. Small hydrogen fires are more difficult to detect and require that certain precautions be taken to avoid personnel and equipment damage. Current fire-detection technology is summarized in a recent document (15) and hydrogen fire detection is reviewed in an older publication (13).

Two types of sensor - thermal and optical - are used to detect hydrogen fires. Thermal sensors are the conventional type and are fully discussed by Custer and Bright (15). These conventional sensors (including smoke and ionization detectors), coupled with flame visibility, are adequate for detection of methane or gasoline fires and not quite adequate for detection of all hydrogen fires. The aerospace industry has advanced the use of optical sensors for detecting hydrogen fires in bright-field environments. The most common optical sensors detect ultraviolet or infrared radiation and several detection schemes exist (13, 15). Closed-circuit infrared and ultraviolet television sets, equipped with appropriate filters, have been successfully used to detect hydrogen fires on rocket engine test stands (18). Intumescent paints have also been used to detect hydrogen fires. The paints char and swell at low temperature (200°C) and emit pungent gases.

Hydrogen fires are obviously more difficult to detect than methane or gasoline fires; however, the availability of modern detection equipment makes it possible to quickly and reliably detect the flames of all three fuels.

Fire-Extinguishment Methods: A brief review of fire extinguishment methods and recommended fire-extinguishment procedures for various combustible materials has been published by the NFPA (19).

The most effective way to combat a hydrogen fire is to allow it to burn itself out. If at all possible, the flow of hydrogen should be shut off by closing a valve between the fire and the source of hydrogen. Attempts should not be made to extinguish the flame by use of water or other extinguishing agents, because the hydrogen is certain to reignite, possibly with explosive violence if it has mixed with air in sufficient amount. This is likely to cause more damage than the fire.

Fire protection systems are necessary, however. The principal fire protection is the separation of equipment by suitable distance and an adequate water-hydrant system which can be used by fire-fighting personnel to cool down adjacent equipment and prevent spread of the fire.

3.13 SELECTION OF PROPER MATERIALS OF CONSTRUCTION

Selection of suitable materials for hydrogen service should take into consideration the following principal criteria:

- Material must be immune to hydrogen embrittlement attack under the use conditions;
- The material must be sufficiently ductile for use at liquid hydrogen temperatures (20.4K);
- The material must permit fabrication of equipment for which leakage is minimum;
- The material must be resistant to elevated temperatures in the event of fire.

Because of a lack of understanding of the basic mechanisms of hydrogen embrittlement, it is found that present designs are based on a variety of empirically determined formulas and that no generally accepted method prevails. Factors upon which present designs of hydrogen equipment are based include -

Nelson charts: These charts are appropriate only for determining the ability of a particular material to withstand hydrogen chemical attack and are not generally applicable to the other hydrogen embrittlement effects described in Section 2.3. A typical Nelson Chart showing safe design conditions for plain carbon steel and carbon steel alloyed with molybdenum is shown in Figure 2.3-1.

A 110k-psi yield strength "rule of thumb": The use of low-yield-strength steels reduces the effects listed in Section 2.3 as hydrogen environment embrittlement and hydrogen stress-cracking. This rule of thumb generally does not apply to the other forms of hydrogen embrittlement.

The use of expensive alloys.

The use of expensive heat-treating and annealing procedures: Here again, heat-treating and annealing are effective in reducing some embrittlement effects, but are not generally applicable to all forms of hydrogen embrittlement.

Over-design: The use of high safety factors.

Test of proposed materials of construction at specific conditions.

The existence of a large number of industrial hydrogen-using processes attests to the ability of present design techniques to handle hydrogen service in most cases, but there are documented cases in which equipment has failed for no discernible reason (20).

The application of the following criteria in the design of hydrogen facilities is suggested in order to avoid hydrogen embrittlement (5):

- Use low-yield-strength steel whenever possible.
- Use heat-treated and fully annealed materials.
- Use careful welding procedures to avoid hard spots and flaws.
- Maintain a careful inspection of all materials for flaws, including voids, inclusions, and hard spots.
- Design for minimum stress levels in all components (particularly cyclic stress).
- Avoid plastic deformation of all materials at all costs.
- Possibly, use an impurity such as oxygen at low concentration levels to control hydrogen stress-cracking and hydrogen environment embrittlement.

Gasketing materials should be of asbestos base or other noncombustible material. Nylon, Teflon, or rubber are not recommended because of their tendency to burn or deform at elevated temperatures.

Valve packings for hydrogen service should be of a material which will not melt or burn. This is another precaution against uncontrolled leakage in the event of fire.

3.14 CRYOGENIC PRECAUTIONS

For service with liquid hydrogen and cold hydrogen gas, care must be taken to choose materials that do not become brittle when cold. Materials selected should retain their ductility even at LH2 temperatures. The approved materials include the austenitic stainless steels (300 series), copper, monel, bronze, brass and aluminum. The stainless steels are preferred and are used most extensively. Aluminum is not generally satisfactory for applications other than liquid containers or portions of a liquid system which are covered by a suitable vacuum jacket or enclosed in an insulated cold box. The intent is to maintain system integrity in the event that the equipment is exposed to a large fire. The relatively low melting point for aluminum could result in piping or vessel failure because of the fire and result in the release of large quantities of hydrogen.

Use of LH2 brings additional possibilities for creating cold surfaces where they are neither expected nor wanted. As mentioned in Subsection 2.3.7, condensation of oxygen enriched air is a potential hazard associated with such cold surfaces. Care must be taken to avoid cooling of auxiliary equipment, either by direct contact with the cold surfaces or by condensed air, so that operating fluids are not frozen or that structural members are not allowed to become brittle or overstressed due to thermal contraction. Also, such cold metal surfaces can present greater burn hazards to personnel than the cryogen itself does. Therefore, it is necessary to thermally insulate system components such as the vent lines that can get cold during either normal or emergency operation. In this case, a vacuum insulation is not required; an externally applied noncombustible foam insulation is required, so that oxygen enrichment within the pores of the foam does not form an explosive mixture in a material that would be normally considered noncombustible or slow burning.

Within cryogenic equipment, large temperature gradients frequently exist which can add thermal stresses to the operating processes. Cryogenic systems must also be cooled down to operating temperatures, and during this cooldown process the mechanism exists for powerful transient cooling stresses. Therefore, a careful analysis and assessment of the thermal stresses that can arise is necessary for the safe design of the cryogenic facility. For example, for long piping systems either there must be sufficient flexibility by means of U-bends and elbows, or the pipe must be provided with expansion bellows.

Also, in the cooldown of cryogenic systems with a cryogenic liquid such as LH2, two-phase flow must be encountered. For low flows such as those required in the cooldown of thick-walled pipes, the two phase can stratify with the liquid flowing at the bottom of the pipe and the gas at the top. The available heat of vapourization (plus the better heat transfer to the liquid) provides a mechanism for the bottom of the pipe to cool faster than the top, thus introducing thermal stresses. To avoid this, care must be taken to limit the flow of the cryogenic cooling fluid within a narrow operating range to maintain nonstratified flow until almost all of the liquid is vaporized. In some cases, there may be no acceptable LH2 cooldown flow, and other methods, such as cold gas precooling, must be employed(2).

3.15 HAZARD IDENTIFICATION AND ASSESSMENT

Another important aspect of hazard aversion consists in the early identification, analysis and assessment of potential hazards, so that counter-measures can be recommended and appropriate methods can be adopted.

A Hazard and Operability Study, or Hazop is a technique recommended and successfully practiced by the industry for the systematic identification of hazards. Hazard Analysis, or Hazan is used to work out the probability of an accident and the extent of the consequences. The essential step in a Hazan consists in breaking down the events leading to the hazard into their constituent parts. The result of the analysis is compared with a target or criterion, so that an assessment of the hazard can be made. Hazop and Hazan can and should be applied to all new designs, and at the design stage.

Hazard identification and assessment techniques are described in Section 5.

4.0 CODES, STANDARDS, REGULATIONS AND RECOMMENDED PRACTICES

NASA, the US Air Force, and several national laboratories have, over the years, compiled their own manuals defining safe practices for the design and operation of liquid and gaseous hydrogen systems. Because much of the liquid hydrogen used in the space program was manufactured far from the sites where it was used, procedures to ensure its safe transportation over public roads and railways had to be developed. The manufacturers, especially Linde, Air Products and Liquid Air, as part of their commercial business of supplying bulk gaseous and liquid hydrogen to industrial customers, have developed their own standards, guidelines, and codes of good practice for the safe production, storage, handling and transport of hydrogen.

From this basis, regulations, standards, and codes concerning the specifications for equipment, shipping regulations, and installation standards for hydrogen containers, road trailers, tank cars and storage stations have been formulated. The equipment specifications outline requirements for the type, size, service pressure, and temperature of the respective vessel. The functional requirements, design details, and manufacturing methods are then established around these equipment specifications. Shipping regulations cover the required operating procedures as they relate to the movement of equipment over the rails and highway. Installation standards provide basic guidelines about functional requirements, performance, and operating characteristics for equipment located on a customer's property. Applicable use of these guidelines provides equipment that will safely contain and distribute hydrogen.

Existing codes and regulations, specifically for hydrogen operations, are mostly concerned with its transportation.

Other phases are covered by more general regulations, and a recent and excellent listing is given by Hord (1),(8). The existing regulations prescribed by law generally make reference to national standards and codes such as ANSI, ASME, ASTM, API, NFPA, CSA, ULC, etc. Industrial insurers invariably specify the ASME code as a condition for insuring facilities with pressure vessels.

4.1 HYDROGEN CODES, STANDARDS AND REGULATIONS - U.S.A.

Various interdisciplinary committees, with industrial, university and government representatives have published guidelines for the safe production and handling of hydrogen. Some of the more substantial documents are listed in Table 4.1. Some of these documents are accepted as national standards and become mandatory and enforceable when specified by regulatory bodies such as the U.S. Department of Transportation (DoT), state and local authorities, etc. Insurance companies usually adopt or specify existing standards, practices and procedures as a condition of insurability for industrial organizations. Examples of nonmandatory standards that may be adopted by regulatory bodies are those issued by the ASME, ANSI, ISA, NFPA, UL, ASTM, etc. Current regulations (mandatory), and codes and standards (non-mandatory) that pertain to hydrogen are listed in Table 4.2.

Federal regulations apply to the interstate transportation of hydrogen and are administered by the various branches of the U.S. Department of Transportation:- the Federal Highway Administration for transport by highway; the Federal Railroad Administration for transport by railway; the Federal Aviation Administration for air transport; and the U.S. Coast Guard for water transport.

The Material Transportation Bureau (through the Office of Hazardous Materials Operations) has enforcement responsibility in all other matters related to vehicular transportation of hydrogen. The Office of Pipeline Safety Operations of the Materials Transportation Bureau has authority over pipeline transmission of hazardous gases and liquids. Title 49 of the Code of Federal Regulations, Parts 102 and 107.301, designates these rule-making and enforcement bodies of the DoT. This regulatory document is cited as 49 CFR 102 and 49 CFR 107.301 (8).

In addition to the regulations and standards set forth in Table 4.2, municipal and state regulations may be imposed for the storage and intrastate transportation of hydrogen.

General industrial safety matters, including the production and handling of flammable compressed and liquefied gases, are regulated by OSHA PL 91-596 Ref.[H5].

4.1.1 Hydrogen Storage

Seamless pressure vessels for storing high-pressure hydrogen are manufactured to the codes of ASME (Code Case 1205); and the requirements of DoL, CTC or DoT, in terms of material specifications, pressure limitations, approved safety devices and retesting apply to the manufacture of cylinders and tubes. Tube-trailer installations must follow the recommendations of CGA and NFPA, as well as those of any local regulatory bodies.

Liquid hydrogen storage vessels are manufactured to the codes and requirements of ASME Section VIII, DoT, NFPA and CFR Title 49.

The applicable codes, standards and safety guidelines for the design and operation of compressed hydrogen and liquid hydrogen storage are included in Tables 4.1 and 4.2.

4.1.2 Hydrogen Distribution/Transmission

A survey of established codes that would apply to the use of hydrogen indicates that both the ANSI code for pressure piping (ANSI B31.8) and the minimum safety standards for transportation of natural and other gases by pipeline of the Department of Transportation (DoT) may be directly applicable to hydrogen distribution systems. In both standards, although the inclusion of gaseous hydrogen is not explicitly spelled out, it is believed to be included on the basis of the standards' definition of "gas". In ANSI B31.8, gas is defined as any gas or mixture of gases suitable for domestic or industrial fuel and transmitted or distributed to the user through a piping system. In DoT's standard, gas means natural gas, flammable gas, or gas that is toxic or corrosive. Since these two standards are the primary codes for natural gas distribution, hydrogen systems seem well covered by the existing specifications and regulations (6).

The National Fire Code, however, has a special section covering the standard for gaseous hydrogen systems at consumer sites. Although the standard does not cover the distribution piping systems and is only specified for hydrogen systems where the hydrogen is delivered by mobile equipment, it is not clear if the standard applies to systems where the hydrogen is delivered to the consumer premises by pipeline. One concern is that in piping, tubing, and fitting design, the standard specifically indicates that cast iron pipe and fittings are not to be used. (The other two national standards contain no such specification.) However, cast iron is not often found in systems to which the National Fire Code applies (6).

Pipeline transmission of flammable compressed gases (presumably including hydrogen) is regulated by CFR Title 49, Parts 190-192.

4.1.3 Hydrogen Transportation

The Transportation Safety Act of 1974 precipitated reorganization of the DoT and concomitant revision of applicable regulatory codes. Equipment specifications and shipping and carrier regulations for gaseous and liquid hydrogen are given in CFR, Title 49, Parts 170-179. This code summarizes the federal regulations for transportation of hydrogen by highway, railroad, air and water. Graziano's [H7] TARIFF No. 32 contains all of the pertinent transportation regulations set forth in Title 49 CFR, except for gas and liquid pipeline regulations- 49 CFR (190-192) and 49 CFR 195, respectively.

The DoT classifies and treats liquid hydrogen as a flammable compressed gas (Part 172.5 of CFR, Title 49). Air transportation of compressed hydrogen gas is regulated by CFR, Title 14, Part 103 and the commercial carrier IATA Tariffs [H6]. Liquid hydrogen is not currently accepted for air shipments.

Transportation of compressed hydrogen gas by water is regulated by CFR Title 49 (172-179) and liquid hydrogen cannot currently be shipped by water; however, the NASA has barged liquid hydrogen over distances of 84 km offshore Louisiana-Mississippi under special permit of the U.S. Coast Guard. The DoT no longer issues "special permits" but grants "exemptions" to the regulations for special shipments of hazardous materials (including liquid hydrogen). The Office of Hazardous Materials Operations of DoT has the authority to issue these exemptions, which are required to transport liquid hydrogen in truck trailers via highway and in all other cases where DoT equipment specifications are non-existent (6) - see CFR (107.1-107.125).

Tables 4.1 and 4.2 list the codes, regulations and safety guidelines pertinent to the transport of gaseous and liquid hydrogen.

4.2 HYDROGEN CODES, STANDARDS AND REGULATIONS - CANADA

The following is a list of codes, regulations and standards governing and/or related to the installation of hydrogen handling systems in Canada. Where specific Canadian codes, standards and regulations do not exist, usually the applicable U.S. codes, standards and regulations are adopted.

A. Gaseous Hydrogen Systems

A.1 NFPA Standard #50A - Gaseous Hydrogen Systems at Consumer Sites

B. Liquefied Hydrogen Systems

B.1 NFPA Standard #50B - Liquefied Hydrogen System at Consumer Sites

B.2 NFPA Standard #30 - Flammable and Combustible Liquid Codes

B.3 NFPA Standard #385 - Standard for Tank Vehicles for Flammable and Combustible Liquids

B.4 NFPA Standard #386 - Standard for Portable Shipping Tanks for Flammable and Combustible Liquids

C. Plant Buildings Housing Hydrogen Operations

C.1 National Building Code

C.2 Provincial Building Code

C.3 Municipal Building Code

C.4 NFPA Standard #220 - Standards on Types of Building Construction

C.5 NFPA Standard #68 - Guide for Explosion Venting

C.6 National Fire Code of Canada

C.7 Provincial Fire Code

C.8 Municipal Fire Code

D. Pressure Vessels Containing Hydrogen

D.1 CSA Standard #B51-M- Code for the Construction and Inspection of Boilers and Pressure Vessels

D.2 ASME Boiler and Pressure Vessel Code Section VIII, Division I

D.3 For the construction of gaseous or liquid hydrogen storage vessels and hydrogen transportation vessels, the regulations of the Provincial Pressure Vessels Department will apply. These generally call for the ASME code.

E. Electrical Systems in Hydrogen Installations

E.1 The Canadian Electrical Code, Part I, CSA Standard #C22.1

E.2 Provincial Regulations

E.3 NFPA Standard #497 - Recommended Practice for Classification of Class I Hazardous Locations for Electrical Installations in Chemical Plants

E.4 NFPA Standard #77 - Recommended Practice on Static Electricity

E.5 NFPA Standard #78 - Lighting Protection Code

E.6 NFPA Standard #493 - Intrinsically Safe Apparatus and Associated Apparatus for Use in Class I, II and III Division I Hazardous Locations

E.7 NFPA Standard #496 - Purged and Pressurized Enclosures for Electrical Equipment in Hazardous (classified) Locations

E.8 CSA-C22.2 No.145 - Motors and Generators for (1972) Use in Hazardous Locations Class I, Groups C and D Class II, Groups E, F and G

E.9 CSA-C22.2 No. 157 - Intrinsically Safe and Non-Incendive Equipment for Use in Hazardous Locations (1979)

F. Hydrogen Piping Systems

F.1 Provincial Regulations

F.2 ANSI/ASME Standard #B31.3 - Code for Chemical Plant and Petroleum Refinery Piping

F.3 CSA Standard #Z184-M - Gas Pipeline Systems

F.4 CSA Standard #Z184S1 - Supplement No. 1 to Z184M (1979)

G. Miscellaneous Standards and Codes

The following standards and codes are not written exclusively for hydrogen systems. However, their contents may be gainfully but judiciously referred to in the design and construction of hydrogen systems, storage and handling equipment.

G.1 CGA Pamphlet #S-1, Parts 1, 2 and 3 - Pressure Relief Device Standards

G.2 ANSI Standard #Z48.1 - American Standard Method of Marking Portable Compressed Gas Containers to Identify the Material Contained

G.3 UL Standard #142 - Standard for Steel Above Ground Tanks for Flammable and Combustible Liquids

G.4 UL Standard #842 - Standard for Valves for Flammable Fluids

G.5 CSA-C22.2 No.152-1976-Combustible Gas-Detection Instruments

H. Transportation of Portable Hydrogen Containers and Cylinders

H.1 The governing body in Canada is Transport Canada (Transport of Dangerous Goods Directorate)

H.2 The governing body in U.S.A. is the Department of Transport (DOT)

H.3 CTC Regulations for the Transportation of Dangerous Goods by Rail, Specifications 3A, 3AA and 3AAX for Hydrogen Cylinders and Hydrogen Tubes used in the construction of tube trailers

H.4 It is important to note that Hydrogen Cylinders and Tubes will soon come under the codes of the Canadian Standards Association, CSA-B-339. Once this code is in effect, the specification will cover both rail and road transportation. At the moment, the CTC Regulations specifically apply to rail movements but are used for road shipments, even though they are not so specified.

H.5 CSA-B332.8-1978 Series 1 Freight Containers-Specification and Testing-Part III: Tank Containers for Liquids and Gases (ISO 1596/111-74).

I. Transportation of Liquid Hydrogen

I.1 Liquid hydrogen transportation equipment - this will, in the future, come under the requirements of CSA-B-339, Specifications for Highway Cargo Tanks. However, at the moment liquid hydrogen trailer designs come under special exemptions in the U.S.; these have been discussed in the U.S. DoT Document HM-115 and will probably be absorbed into the U.S. Regulations once HM-115 has been approved. Until such time as a specification is included in CSA-B-338, industry is anticipated to work with the U.S. Regulation and the Provincial Government's, under the overall policies of the Transport of Dangerous Goods Branch, Transport Canada, in Ottawa.

J. Codes of Good Practice

In addition to the above regulations, the appropriate practices laid out in the various Compressed Gas Association pamphlets should be adhered to. These would include the following:

CGA Pamphlet No.	Title
C-1	Methods for Hydrostatic Testing of Compressed Gas Cylinders
C-2	Recommendations for the Disposition of Unserviceable Compressed Gas Cylinders
C-4	Method of Marking Portable Compressed Gas Containers to Identify the Material Contained
C-5	Cylinder Service Life Seamless High Pressure Cylinders
C-6	Standards of Visual Inspection of Compressed Gas Cylinders
C-7	Precautionary Labelling and Marking of Compressed Gas Cylinders
C-10	Recommendations for Changes of Service for Compressed Gas Cylinders
C-11	Recommended Practices for Inspection of Compressed Gas Cylinders at Time of Manufacture
C-14	Procedures for Fire Testing of DOT Cylinder Safety Relief Device Systems

C-15	Procedures for Cylinder Design Proof and Service Performance Tests
G-5	Hydrogen
G-5.3	Commodity Specification for Hydrogen
P-1	Safe Handling of Compressed Gas in Containers
P-6	Standard Density Data Atmospheric Gases in Hydrogen
P-7	Standard for Requalification of Cargo Tank Hose used in the Transfer of Compressed Gases
P-11	Metric Practice Guide for the Compressed Gas Industry
P-12	Safe Handling of Cryogenic Liquids
S-1.1	Pressure Relief Device Standards Part I - Cylinders for Compressed Gases
S-1-2	Pressure Relief Device Standard Part II - Cargo and Portable Tanks for Compressed Gases
S-1-3	Pressure Relief Device Standards Part III - Compressed Gas Storage Containers
V-1	American National Standard, Canadian Standards Association and Compressed Gas Association Standard Compressed Gas Cylinder Valve Outlet and Inlet Connections: ANSI B57.1 CSA B96
V-6	Standard Cryogenic Liquid Transfer Connections
V-7T	Tentative Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures
CGA-341	Tentative Standard Insulated Tank Truck Specifications CGA-341 for Cold Liquefied Gases

TABLE 4.1: HYDROGEN SAFETY AND EQUIPMENT GUIDELINES (NONMANDATORY) - U.S.A.

SAFETY ITEM	REFERENCES **
Handling procedures (includes safety in production, transportation & distribution, personnel training, etc.	A1 - A25
Storage	A1, A16, A17, A21, A22, A23, B1
Explosive Criteria	Summarized in A1 and C1 See also C2 and C3
Leak & Fire Detection, Prevention, Control	D1-D6, A1, G4 & G5
Facilities	A1 and C1
Mechanical Equipment	F1-F18
Electrical Equipment	G1-G10

** The References are listed in Table 4.3.

TABLE 4.2: REGULATIONS (MANDATORY) FOR DISTRIBUTION OF HYDROGEN IN THE U.S.A.

DISRTIBUTION OF HYDROGEN BY	EQUIPMENT SPECIFICATIONS	TRANSPORTATION REGULATIONS
Cylinders filled with liquid (< 1000 pounds water capacity) - by highway only	CFR, Title 49, Part 178.57 Ref. [H2]	CFR, Title 49, Parts 173.316, 177.823, 177.840 Ref. [H2]
Railway tank cars filled with liquid	CFR, Title 49, Parts 179.400, 179.401, Ref. [H2]	CFR, Title 49, Part 173.316, Ref. [H2]
Highway truck trailers filled with liquid	CGA*-341 and DoT Approval prior to fabrication Ref. [F17]	Special permit from Hazardous Materials Regulation Board of DoT (see CFR, Title 49, Parts 173.33, 177.823) Ref. [H2]
Container filled with liquid - by air or waterway	-----	Not allowed under current regulations (see CFR, Title 14, Parts 103.7, 103.9 and CFR, Title 46, Part 146.24), Ref's. [H3, H4]. Shipment by tank barge has been allowed under special permit of the U.S. Coast Guard Commandant.
Liquid pipeline	ANSI B31.8, B31.3*, B31.10*, Ref's [H1,F5,F6]	CFR, Title 49, Parts 190-192, Ref. [H2]
Cylinders filled with compressed gas - by highway or rail	CFR, Title 49, Parts 173.34, 178.36, 178.37 Ref. [H2]	CFR, Title 49, Parts 173.302, 176.703, 177.823, Ref. [H2]

TABLE 4.2: REGULATIONS (MANDATORY) FOR DISTRIBUTION OF HYDROGEN IN THE U.S.A. (continued)

DISRTIBUTION OF HYDROGEN BY	EQUIPMENT SPECIFICATIONS	TRANSPORTATION REGULATIONS
Railway tank cars filled with compressed gas	CFR, Title 49, Parts 173.31, 179.500 Ref. [H2]	CFR, Title 49, Parts 173.314, Ref. [H2]
Highway truck trailers filled with compressed gas	CFR, Title 49, Parts 173.34, 178.36, 178.37 Ref. [H2]	CFR, Title 49, Parts 173.301, 173.302 177.823, Ref. [H2]
Container filled with compressed gas - by air	CFR, Title 49, Parts 173.34, 178.36, 178.37 Ref [H2]	CFR, Title 14, Part 103.9, ref. [H4]. Dot approved cylinder on cargo aircraft only, with a maximum charge of 300 pounds (136 kg) of H2 per cylinder. See also CAB No. 82 Ref's [H2, H6]
Container filled with compressed gas - by waterway	CFR, Title 49, Parts 173.31, 173.34, 178.36 178.37, 179.500 and CFR, Title 46, Part 146.24, Ref's [H2, H3]	CFR, Title 46, Part 146.24. DoT approved cylinders on cargo vessels only and DoT approved railway tank cars on trainships only, Ref. [H3].
Gas pipeline	ANSI B31.8, B31.3* Ref's [H1, F5]	CFR, Title 49, Parts 190-192 Ref. [H2]

TABLE 4.2: REGULATIONS (MANDATORY) FOR DISTRIBUTION OF HYDROGEN IN THE U.S.A. (continued)

Storage of Hydrogen at Consumer Sites as	Equipment Specifications	Industrial Standards
Compressed gas	ASME*, Section VIII.	NFPA* 50A, Ref.[A21] Divisions 1 and 2 Ref's. [F1, F2]
Liquid	ASME*, Section VIII.	NFPA, 50B, Ref.[A22] Divisions 1 and 2 Ref's. [F1, F2]

General industrial safety matters, including the production and handling of flammable, compressed, and liquefied gases, are regulated by OSHA PL 91-596 Ref.[H5].

*Not mandatory but industrially accepted standards, in the U.S.A.

Note: The References are listed in Table 4.3.

TABLE 4.3: REFERENCES TO TABLES 4.1 AND 4.2

Note: In the references that follow,

CGA	Compressed Gas Association, Inc., 1235 Jefferson Davis Highway, Arlington, Va. 22202.
ANSI	American National Standards Institute, 1430 Broadway, New York, NY 10018
NFPA	National Fire Protection Association, Publication Sales Department, 470 Atlantic Ave., Boston, MA 02210
ASME	American Society of Mechanical Engineers, United Engineering Center, 345 East 47th Street, New York, NY 10017
UL	Underwriters' Laboratories, Publication Stock, 333 Pfingsten Road, Northbrook, IL 60062
ISA	Instrument Society of America, 400 Stanwix Street, Pittsburg, PA 15222

[A1] General Safety Engineering Design Criteria, Vol. 1 CPIA public. 194, (October 1971); also, Liquid Propellant Handling, Storage and Transportation, Vol. 3, CPIA public. 194 (May 1972) - documents prepared by the JANNAF propulsion committee of the JANNAF Hazards Working Group and are available from the Chemical Propulsion Information agency (CPIA) of the John Hopkins University Applied Physics Laboratory, 8621 Georgia Avenue, Silver Spring, MD 20910; (also available to the public through National Technical Information Service Springfield, VA 22150: Vol. 1 Accession No. AD 889 763 Vol. 3 Accession No. AD 870 259).

[A2] Hydrogen Safety Manual, NASA Lewis Research Center, NASA Tech. Memo TM-X-52454 (1968)

[A3] On an investigation of hazards associated with the storage and handling of liquid hydrogen, Final Report C-61092, Contract No. AF 18(600) - 1687, prepared by Arthur D. Little Inc., DDC Access. No. AD 324194, 137 pp. (Mar. 1960)

[A4] Liquid hydrogen, a guide for the safe handling and storage of liquid hydrogen at LASL Facilities, Los Alamos Scientific Laboratory, P.O. Box 1663 Los Alamos, NM 87544

[A5] Weintraub, A.A., Control of liquid hydrogen hazards at experimental facilities: a review, health and safety laboratory, U.S. Atomic Energy Comm., New York, NY (May 1965); also, Grumer, J., Strasser A., and Van Meter, R.A., Principles for safe handling of liquid hydrogen, Bur. of Mines Tech. Rept. (June 1967)

[A6] Chelton, D.B., Safety in the use of liquid hydrogen, Book, Technology and Uses of Liquid Hydrogen, Ed. by R.B. Scott, W.H. Denton, and C.M. Nicholls, pp. 359-378 (The Macmillan Co., New York 1964)

[A7] Connolly, W.W., A practical safety standard for commercial handling of liquefied hydrogen, Book, Advances in Cryogenic Engineering 12, Ed. by K.D. Timmerhaus, pp. 192-197, (Plenum Press, New York, 1967)

[A8] Recommended materials and practices for use with cryogenic propellants, Aerospace Information Report, AIR 839B, 68 pp. (Society of Auto. Engrs., Apr. 1969)

[A9] Cryogenics safety manual, a guide to good practice, (British Cryogenics Council, 16 Belgrave Square, London, SWIX8PT, 1970)

[A10] Hernandez, H.P., Safety guidelines for accelerator installations, Lawrence Radiation Laboratory Rept. No. UCRL-18555 (Feb. 1969)

[A11] Handbook of Compressed Gases, Compressed Gas Association Inc., (Rheinhold Publishing Corp. New York, 1966)

[A12] Safe Handling of Compressed Gases in Containers, CGA Pamphlet P-1

[A13] Method of Marking Portable Compressed Gas Containers to Identify the Material Contained, CGA Pamphlet C-4; also ANSI Z48.1-1954 (R-1971)

[A14] Guide to the Preparation of Precautionary Labeling and Marking of Compressed Gas Containers, CGA Pamphlet C-7

[A15] Hydrogen, CGA Pamphlet G-5

[A16] Standard for Gaseous Hydrogen at Consumer Sites, CGA Pamphlet G-5.1.

[A17] Standard for Liquefied Hydrogen Systems at Consumer Sites, CGA Pamphlet G-5.2.

[A18] Commodity Specification for Hydrogen, CGA Pamphlet G-5.3; see also, Hydrogen Commodity Specification, MIL-P-272013 (June 1971); available from USN Supply Depot, 5801 Tabor Ave., Philadelphia, PA 19120).

[A19] Lightning Protection Code, NFPA Pamphlet No. 78 (ANSI C5.1).

[A20] Static Electricity, NFPA Pamphlet No. 77

[A21] Standard for Gaseous Hydrogen Systems at Consumer Sites, NFPA Pamphlet No. 50A (ANSI Z292.2)

[A22] Standard for Liquefied Hydrogen Systems at Consumer Sites, NFPA Pamphlet No. 50B (ANSI Z292.3)

[A23] Standard for the Installation and Operation of Oxygen-Fuel Gas Systems for Welding and Cutting, NFPA Pamphlet No. 51; see also, Standard on Safety in Welding and Cutting, ANSI Z49.1

[A24] Siewert, R.D., Evacuation areas for transportation accidents involving propellant tank pressure bursts, NASA TMX-68277 (Nov. 1972)

[A25] Emergency services guide for selected hazardous materials (spills, fire, evacuation area), Dept. of Transportation, Office of the Secretary, Office of Hazardous Materials, Washington, D.C. 20590 (Apr. 1974)

[B1] Zabetakis, M.G., and Burgess, D.S., Research on the hazards associated with the production and handling of liquid hydrogen, Bureau of Mines Report, RI-5707 (1961)

[C1] Hord, J., Explosion criteria for liquid hydrogen test facilities, Nat. Bur. stand. (U.S.), NBS Report (Feb. 1972)

[C2] Explosion Venting, NFPA Pamphlet no. 68

[C3] Explosion Prevention Systems, NFPA Pamphlet no. 69

[D1] Rosen, B., Dayan, V.H.,and Proffit, R.L., Hydrogen leak and fire detection, NASA SP-5092 (1970)

[D2] Automatic Fire Detectors, NFPA Pamphlet No. 72E

[D3] Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids, NFPA Pamphlet No. 325M

[D4] National Fire Codes, NFPA Volumes 1 and 2 (general fire-fighting and fire control).

[D5] Donnini, J.M., Hydrogen fire blink detector, U.S. Patent Application S/N 51477 (July 1970)

[D6] Custer, R.L.P., and Bright, R.G., Fire detection: the state of the art, Nat. Bur. Stand. (U.S.) Tech. Note TN-839 (June 1974)

[F1] ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, Pressure Vessels: this reference applies to gaseous and liquid containers for portable and stationary applications.

[F2] ASME Boiler and Pressure Vessel Code, Section VIII, Division 2, Pressure Vessels: Alternative Rules: this reference applies to gaseous and liquid containers for stationary applications only.

[F3] ASME Boiler and Pressure Vessel Code, Section IX, Welding and Brazing Qualifications.

[F4] ASME Boiler and Pressure Vessel Code, Section III, Nuclear Power Plant Components: a series of standards applicable to nuclear plants and installations.

[F5] American National Standard Code for Pressure Piping, Petroleum Refinery Piping, ANSI B31.3, (ASME, New York): this reference applies to gaseous and liquid piping.

[F6] American National Standard Code for Pressure Piping, Cryogenic Piping System, ANSI B31.10 (in preparation)

[F7] Vacuum insulated cryogenic pipes, some recommendations concerned with pipe and coupling design, (British Cryogenics Council, 16 Belgrave square, London SWIX 8PT, 1972).

[F8] Safety Relief Device Standards, Part 1 - Cylinders for Compressed Gases, CGA Pamphlet S-1.1; Part 2 - Cargo and Portable Tanks for Compressed Gases, CGA Pamphlet S-1.2; Part 3 - Compressed Gas Storage Containers, CGA Pamphlet S-1.3.

[F9] Recommended Practice for the Manufacture of Fusible Plugs, CGA Pamphlet S-4

[F10] Frangible Disc Safety Device Assembly, CGA Pamphlet S-3.

[F11] Compressed Gas Cylinder Valve Outlet and Inlet Connections, CGA Pamphlet V-1 (also Canadian Standards Association CSA B96 and American National Standards Institute ANSI B57.1.

[F12] Methods for Hydrostatic Testing of Compressed Gas Cylinders, CGA Pamphlet C-1.

[F13] Standards for Welding and Brazing on Thin Walled Containers, CGA Pamphlet C-3.

[F14] Cylinder Service Life, Seamless, High-Pressure Cylinder Specifications ICC-3, ICC-3A, ICC-3AA, CGA Pamphlet C-5.

[F15] Standards for Visual Inspection of Compressed Gas Cylinders, CGA Pamphlet C-6.

[F16] Standard for Requalification of DoT-3HT Cylinders, CGA Pamphlet C-8

[F17] Tentative Standard for Insulated Tank Truck Specification for Cold Liquefied Gases, CGA Pamphlet CGA-341

[F18] Voth, R.O., Safety of hydrogen pressure gauges, Book, Advances in Cryogenic Engineering, 17, Ed. by K.D. Timmerhaus, pp. 182-187 (Plenum Press, New York, 1972).

[G1] Standard for Intrinsically Safe Apparatus for Use in Class I Hazardous Locations, NFPA Pamphlet No. 493

[G2] Standard for Purged and Pressurized Enclosures for Electrical Equipment in Hazardous Locations, NFPA Pamphlet No. 493

[G3] National Electrical Code, Chap. 5, Articles 500-501, NFPA Pamphlet No. 70.

[G4] Fire Protection Equipment Directory (Jan. 1977), available from UL.

[G5] Hazardous Location Equipment Directory (Jan. 1977), available from UL.

[G6] Electrical Instruments in Hazardous Atmospheres, ISA-RP 12.1 (1960)

[G7] Intrinsically Safe and Non-Incendive Electrical Instruments, ISA-RP 12.2 (1965)

[G8] Instrument Purging for Reduction of Hazardous Area Classification, ISA-S12.4 (1970)

[G9] Electrical Safety Practices, ISA Monograph 113 (1972)

[G10] Magison, E.C., Electrical Instruments in Hazardous Locations, 2nd edition, Book, 321 pp. (Instrument Society of America, Pittsburgh, Pennsylvania, 1972)

[H1] American National Standard Code for Pressure Piping, Gas Transmission and Distribution Piping Systems, ANSI B31.8

[H2] Code of Federal Regulations, Title 49, Transportation, Parts 100 to 199, U.S. Government Printing Office, Washington D.C. 20402

[H3] Code of Federal Regulations, Title 46, Shipping, Parts 140 to 149, U.S. Government Printing Office, Washington, D.C. 20402

[H4] Code of Federal Regulations, Title 14, Aeronautics and Space, Parts 60 to 199, U.S. Government Printing Office, Washington, D.C. 20402.

[H5] Occupational Safety and Health Act of 1970, PL 91-596 (Dec. 29, 1970) in United States Statutes at Large, 91st Congress, Second Session, 84, Part 2, pp. 1590-1620, (U.S. Government Printing Office, Washington, D.C. 20402, 1971).

[H6] Official Air Transport Restricted Articles Tariff No. 6-D, Civil Aeronautics Board (CAB) No. 82, Section I (pp. 14-15), Section II (p. 53) and Section III - Part A (p. 94), issued by the Airline Tariff Publishing Company, Dulles International Airport, P. O. Box 17415, Washington, D.C. 20041.

[H7] R.M.Graziano's TARIFF No. 32 (with supplements), Hazardous Material Regulations of the Department of Transportation by Air, Rail, Highway, Water and Military Explosives by Water including Specifications for Shipping Containers, published by Bureau of Explosives, Association of American Railroads, 1920 L Street, N.W., Washington, DC 20036 (November 1978).

5. HAZARD IDENTIFICATION AND ASSESSMENT

The search for prospective problems begins with a potential cause, which leads to deviations which lead to a consequence. It is impossible to eliminate all hazards in a plant or system, but for safety's sake all potential ones must be identified and evaluated. Until a hazard has been identified, no counter-measures can be proposed. The most fundamental of all methods of hazard identification is experience. The result of this experience is then embodied in a series of codes or standards. Checklists are also often used to identify hazards and problems that make operations difficult. Checklists may be satisfactory if there is little or no innovation, and all the hazards have been met before; they are least satisfactory when the design and application are new. Moreover, checklists have an inherent disadvantage in that any missing items are never brought up, so our minds are closed to them. One supplementary approach which has been preferred and used with great success by the chemical process industry during the design stage of process plants is known as a "Hazard and Operability Study", or "Hazop". This is a systematic, yet creative or open-ended approach which enables a multidisciplinary team to visualize hazards at various stages during the design (29). The technique provides opportunities for people to let their imaginations go free and think of all possible ways in which hazards or operating problems might arise. But to reduce the chance that something will be missed, it is done in a systematic way, each component and each sort of hazard being considered in turn. Thus, it allows those expert in the process to bring their knowledge and experience to bear systematically, component-by-component, deviation-by-deviation so that problems are less likely to be missed. A hazop is no substitute for knowledge and experience. It merely harnesses the knowledge and experience of the team in a systematic and concerted way.

A detailed account of various hazard and operability studies and hazard analyses are found in References (23-32).

5.1 GENERAL APPROACH TO HAZARD IDENTIFICATION

The Hazard and Operability Study Procedure consists of the following steps:

Definition : Describe the area of study, the hazards to be looked for, the team membership and authority.

Preparation: Assemble the necessary data, prepare a plan and a schedule of meetings.

Examination: Identify hazards.

Follow-up : Deal with the hazards

The distinguishing features of Hazard and Operability Studies are the methods employed during the examination stage to identify hazards. There are three approaches adopted during the examination stage, namely:

- Create a data base of material properties by using a checklist.
- Apply a checklist to a block layout to identify broad-scale hazards.
- Apply what is called a "Guide Word" approach to a detailed schematic design.

A Data Base of Material Properties: We know that many of the materials used or produced in the Process Industries have properties which are hazardous or which could cause nuisances. Hazards such as "Fire", "Explosion", "Toxicity" or nuisances such as "Dust" or "Smell". If a comprehensive checklist is applied to all the materials likely to be present in a unit we should detect all the hazards and nuisances which are inherent properties of the materials themselves, in the physical conditions in which they will be present. In addition to a qualitative description of hazards and nuisances, it is possible to record quantitative measurements of the intensity of hazards. Thus the Hazard "Fire" can lead, not only to a note that a material is flammable, but a record made of the various numerical measurements associated with fire, such as flammable limits, flash point and auto ignition temperature. A note can also be made of data which are lacking and steps can be initiated to obtain the required information.

A "Creative Checklist" Hazard & Operability Examination: This also uses a checklist of hazards and nuisances. In this type of examination, each item in the checklist is applied to large scale parts of a unit in the form of a block layout. Thus the association of, say, a storage unit with "Fire" creates an "image" of that unit on fire. The properties of the materials contained within the unit will have already been established during the preparation of the data base. Thus an assessment of the likelihood of a fire can be made and the need for countermeasures recorded.

The flow of hazards can be two-way. For example, although a liquid nitrogen storage is not likely to catch fire, the consequences of an adjacent fire could be serious. If all items on the checklist are applied to all parts of a block layout, all hazards associated with the individual parts, together with the potential for adverse interactions or "domino effects" should be identified. In addition, hazardous interactions between the unit and its environment should also be identified.

A Guide Word Hazard and Operability Examination: This method of hazard identification is based on the assumption that all "intrinsic" hazards are caused by deviations from the intentions of designers. By "intrinsic" hazards is meant, hazards caused by maloperation or malfunction of small parts of the unit itself. Notional or hypothetical deviations can be generated by distinctive words or phrases called "Guide Words" and the procedure built around this is called "Guide Word" Hazard and Operability Examination.

The distinctive ways in which any part of the design can depart from its "designed intention" can be associated with a distinctive word or phrase called "Guide Words". If, therefore, all possible sets of Guide Words are applied to a single part of a design, a climate of imaginative thinking should be created in which all possible deviations and associated hazards should be detected. If this sequence is repeated for all parts of the design, all possible hazards should be identified.

Thus "Guide Words" are applied to the design intention. The design intention tells us what the equipment or part is expected to do. Table 5.1 is a list of such "Guide Words".

TABLE 5.1 A LIST OF GUIDE WORDS

GUIDE WORDS	MEANINGS	COMMENTS
NO or NOT	The complete negation of these intentions	No part of the intentions is achieved but nothing else happens
MORE LESS	Quantitative increases or decreases	These refer to quantities + properties such as flow rates and temperatures as well as activities like 'HEAT'and 'REACT'
AS WELL AS	A qualitative increase	All the design and operating intentions are acheived together with some additional activity
PART OF	A qualitative decrease	Only some of the intentions are achieved; some are not
REVERSE	The logical opposite of the intention	This is mostly applicable to activities, for example reverse flow or chemical reaction. It can also be applied to substances, e.g. 'POISON' instead of 'ANTIDOTE' or 'D' instead of 'L' optical isomers
OTHER THAN	Complete substitution	No part of the original intention is achieved. Something quite different happens

5.2 ANALYSIS AND ASSESSMENT OF HAZARDS

In the development of a design, the hazard and operability study comes first. The hazards and problems that can prevent efficient operation are identified. After identifying the hazards, an assessment of the hazards is necessary to determine the extent to which one should go in removing them or in protecting people and property,and to propose suitable counter-measures. However, if there is an obvious major hazard, a hazard analysis can be started even before the hazard and operability study is carried out.

There are several methods in use for assessing hazards. Sometimes, there is a cheap and obvious way of eliminating the hazard; sometimes the assessment is based on experience or a code of practice. Some of the commonly used hazard analysis methods include:

- Failure Analysis
- Fault Trees Analysis
- Hazard Analysis or Hazan

5.2.1 Failure Analysis

Failure analysis is described by Leech (61). The following questions are posed:-

What failure are we considering?
What is the result of the failure?
How is the failure indicated?
What should be done if a failure is indicated?
Can we accept the situation?

A failure analysis is a comparatively crude criterion of acceptance. If the system is acceptable after such analysis then the overall reliability can be calculated from the reliability of components and consideration given to parts of low reliability being duplicated to build in redundancy. These techniques can be applied to whole plants if the treatment is very general. Better results are obtained when considering individual units and their control, instrumentation and alarms.

5.2.2 Fault Tree Analysis

A fault tree is a logic diagram identifying the event sequence which could lead to a specified failure event. They are widely used in hazard analysis to set down, in a logical way, the events leading to a hazardous occurrence. They allow us to see the various combinations of events that are needed and the various ways in which the chain of events can be broken. They allow us to calculate the probability of the hazardous event from other probabilities that are known. The key components of the fault tree are logic gates. The points at which two branches of a fault tree join are known as gates; they can be "AND" or "OR" gates. The 'AND' gate transmits an output event if one or more of the input events are present. Other types of gate are possible. Figure 6.1 is a fault tree diagram which indicates some of these characteristics. The primal events cause failure sequences which lead to the hazard event of interest.

For a description of this procedure as applied to a chemical plant, see Powers and Tompkins (123), who have developed computer programs using Boolean algebra to describe the unit models.

Estimating hazard rates is not the only use of fault trees. They help us think out all the ways in which the hazard can arise and they show us which branches of the tree contribute the most toward the hazard rate. They show us how we can reduce the hazard rate and which methods will be most effective.

5.2.3 Hazard Analysis, or Hazan

Hazard Analysis, or Hazan is the term used to describe the application of numerical methods to safety problems. It consists of methods that can be adopted to provide quantitative measures to judgements that are usually qualitative in nature.

When it is less easy to assess the hazard and decide on the method of eliminating the hazard, the probability of an accident and the extent of the consequences need to be worked out. These are then compared with a target or criterion. This method is known as "Hazard Analysis" or "Hazan". Sometimes, a few minutes of estimation is sufficient; on other occasions, detailed studies taking many weeks may be necessary. The analysis may involve construction of several fault trees, analysing each event, and estimating the probability that various major events of interest will occur. Hazard Analysis is described by Lawley and Kletz (23, 25, 26, 27).

Every hazard analysis consists of three steps:

- Estimating how often the incident will occur.
- Estimating the consequences to:
    - o Employees
    - o Members of the public
    - o Plants and profits
- Comparing the results of (1) and (2) with a target or criterion, in order to decide whether or not action to reduce the probability of occurrence or minimize the consequence is desirable, or whether the hazard can be ignored (at least for the time being).

In both (1) and (2), estimates should be based, whenever possible, on past experience. However, sometimes there is no past experience, either because the design is new or the incident has never happened, and in these cases we must use synthetic methods.

In brief, the stages in hazard analysis are:

o How often? o How big? o So what?

5.2.4 Limitations of Hazop and Hazan

Most errors in hazard analysis are not due to errors in the data but to errors in drawing the fault tree - that is, to a failure to foresee all the ways in which the hazard could arise. Time is usually better spent looking for all the sources of hazard than in quantifying with greater precision those that have already been found.

One of the serious pitfalls of hazard analysis is that the data may be inapplicable. If the available data is used without checking that the conditions are

> similar, serious errors may be introduced. Design changes may make the data, that was applicable in the past, inapplicable. Changes in the maintenance policy may also affect the validity of the data. The reliability of the personnel (designers, operators etc.) is the most difficult parameter to quantify with any degree of certainty. In a hazard and operability study the operability part is as important as the hazard part. In most studies, more operating problems are identified than hazards. The Hazop and Hazan techniques assume that management is competent, and that the plant will be operated and maintained in the manner assumed by the design team and in accordance with good management and engineering practice. In particular, it is assumed that protective systems will be tested regularly and, when necessary, repaired promptly.

In summary, hazard assessment techniques are used throughout the life cycle of the plant to determine:

- whether a risk is perceived or real,
- the degree of protection required, and
- the most cost effective alternatives for improving process safety.

Although there are limitations to the application of these techniques, industries have come to rely increasingly on quantitative methods for hazard assessment.

The use of hazard assessment enables management to apply resources where most needed. It also facilitates making rational decisions regarding the degree of protection needed. Furthermore, hazard assessment techniques give a rational basis to determine which safety related improvements should be done first to achieve the greatest improvement.

REFERENCES

1. Hord, J., "Is Hydrogen Safe?", NBS Technical Note 690, National Bureau of Standards, Boulder, Colorado, October 1976.

2. Edeskuty, F.J., "Hydrogen: Its Technology and Implications", Chapter 5, Safety; CRC Press.

3. Chelton, D.B., "Safety in the Use of Liquid Hydrogen", Cryogenic Engineering Laboratory, National Bureau of Standards, Boulder, Colorado.

4. Kalyanam, K.M., Lyle, A.R., "Bulk Storage of Hydrogen", Under a Contract from the National Research Council of Canada- No. DSS-01SX. 31155-2-2602, July 1984.

5. Stephen Foh, Martin Novil et. al.," Underground Hydrogen Storage", Final Report, Institute of Gas Technology, Project 65013.

6. Gregory, D.P., "A Hydrogen-Energy System", American Gas Association, August 1972.

7. CGA Pamphlet G-5, "Hydrogen", Compressed Gas Association, Inc.

8. Hord, J., "Hydrogen Safety: An annotated Bibliography of Regulations, Standards and Guidelines," International Journal of Hydrogen Energy, vol. 5, No. 6, pp. 579-584, 1980

9. Hord, J., "Explosion Criteria for Liquid Hydrogen Test Facilities", National Bureau of Standards (U.S.), unpublished report (Feb. 1972)

10. "General Safety Engineering Design Criteria," Vol. 1, CPIA Publication 194 (Oct. 1971), and "Liquid Propellant Handling, Storage and Transportation, Vol. 3, CPIA Publication 194 (May 1972)

11. W.E. Baker, V.B. Parr, R.L. Bessey and P.A. Cox "Assembly and Analysis of Fragmentation Data for Liquid Propellant Vessels", NASA CR-134538 (January 1974)

12. W.E. Baker, J.J. Kulesz, et al, "Workbook for Predicting Pressure Wave and Fragment Effects of Exploding Propellant Tanks and Gas Storage Vessels", NASA CR-134906 (Nov. 1975)

13. Rosen, B., Dayan, V.H., and Proffit, R.L., "Hydrogen Leak and Fire Detection, a Survey", NASA SP-5092, 1970

14. Marr, J.W., "Leakage Testing Handbook", NASA CR-952, April 1968.

15. Custer, R.L.P., and Bright, R.G., "Fire Detection: the State-of-the-art", NASA CR-134642. NBS TN-839, June 1974.

16. Howard, W.B. et al., "Flame Arresters for High-hydrogen Fuel-air Mixtures", Loss Prevention 9, American Institute of Chemical Engineers, 1975.

17. R.D. Witcofski, J.E. Chirivella, "Experimental and Analytical Analyses of the Mechanisms Governing the Dispersion of Flammable Clouds Formed by Liquid Hydrogen Spills", Hydrogen Energy Progress - IV, Vol. 4., June 1982.

18. Edeskuty, F.J., Henshall, J.B., and Barlitt, J.R. "Cryogenics in the Nuclear Rocket Program", Cryogenics and Industrial Gases, June 1969.

19. "Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids", NFPA Pamphlet NO. 325M, 1969.

20. Ordin, P.M., "Review of Hydrogen Accidents and Incidents in NASA Operations," paper presented at the 9th International Energy Conversion Engineering Conference. San Francisco, August 26-30, 1974.

21. N.H.G. Daniels, B.C. Syrett and R.L. Jones, Materials requirements for advanced energy systems. New Fuels. Vol. 3, Materials research needs in advanced energy systems using new fuels, Final Report ARPA-2484, Contract No. DAHC15-73-C-0313, prepared by Stanford Research Institute, 110 pp. (July 1974), available through National Technical Information Service, Springfield, VA 22150, DDC Accession No. AD A004550.

22. J.G. Hust, survey of materials for hydrogen service, Chapter 4, in NBS Special Publication, Selected Topics on Hydrogen Fuel, Ed. by J. Hord, NBS SP-419 (May 1975), available from U.S. Government Printing Office, Washington, DC 20402.

23. "Hazard and Operability Studies", Chemical Industries Association, London, 1977.

24. Knowlton, R.E., "An Introduction to Hazard and Operability Studies," Chemetics International, Vancouver, 1981.

25. Kletz, T.A. "Hazop and Hazan - Notes on the Identification and Assessment of Hazards, "Institution of Chemical Engineers, London, 1983.

26. Lawley, H.G. Hydrocarbon Process, Vol. 55, No. 4, p. 247, April 1976, Reprinted in Vervalin, C.H. ed., "Fire Protection Manual for Hydrocarbon Processing Plants," Vol. 2, p. 94, Gulf Publishing Co., Houston, Tex., 1981.

27. Kletz, T.A. and Lawley, H.G., in "High Risk Safety Technology," ed. by Green, A.E., Chapter 2.1, Wiley, London, 1982.

28. Kletz, T.A., "Eliminating Potential Process Hazards," Chemical Engineering, pp. 48-68, vol. 92, No. 7, April 1, 1985.

29. "Hydrogen Safety - An Assessment of the Safety Problems Associated with the use of Hydrogen as a Ground Transportation Fuel", Chemetics International Company, 1983.

30. Flowsheeting for Safety - A guide on Safety Measures to Consider during the Design of a Chemical Plant", the Institute of Chemical Engineers, Warwickshire, England.

31. Leech, D.J., "Management of Engineering Design", Wiley, 1972.

32. Powers, G.J. and Tompkins, F.C., 1973, Synthesis Strategy for Fault Trees in Chemical Processing Systems, CEP Loss Prevention, Vol. 8, 91.

33. Mikolowsky, W.T., and Noggle, L.W., The potential of liquid hydrogen as a military aircraft fuel, Proc. of the 1st World Hydrogen Energy Conf., Miami Beach, Florida, Vol. III, Ed. by T.N. Veziroglu, Paper 5C-31 (March 1976).

34. Bowen, T.L., Investigation of hazards associated with using hydrogen as a military fuel, report 4541, Naval Ship Research and Development Center, Bethesda, MD 20084 (Aug. 1975).

35. Strehlow, R.A., and Baker, W.E., "The Characterization and evaluation of accidental explosions", NASA CR-134779 (June 1975); (available from National Technical Information Service, Springfield, Va 22151).

36. Edeskuty, F.J., et al., "A guide for the Safe Use of Hydrogen", Report prepared for Ontario's UTDC, No. 325-CR-701-105.

APPENDIX A

Physical and Chemical Properties of Hydrogen, Methane and Gasoline

APPENDIX A: Physical and Chemical Properties of Hydrogen, Methane and Gasoline*** (Ref. 1)

PROPERTY	HYDROGEN	METHANE	GASOLINE
Molecular weight	2.016	16.043	~ 107.0
Triple point pressure, atm	0.0695	0.1159	-
Triple point temperature, K	13.803	90.680	180 - 220
Normal boiling point (NBP) temperature, K	20.268	111.632	310 - 478
Critical pressure, atm	12.759	45.387	24.5- 27
Critical temperature, K.	32.976	190.56	540 - 569
Density at critical point, g/cc	0.0314	0.1604	0.23
Density of liquid at triple point, g/cc	0.0770	0.4516	-
Density of solid at triple point, g/cc	0.0865	0.4872	-
Density of vapor at triple point, g/cu.m	125.597	251.53	-
Density of liquid at NBP, g/cc	0.0708	0.4226	~ 0.70
Density of vapor at NBP, g/cc	0.00134	0.00182	~ 0.0045
Density of gas at NTP, g/cu.m	83.764	651.19	~ 4400
Density ratio: NBP liquid-to-NTP gas	845	649	~ 156
Heat of fusion, J/g	58.23	58.47	161
Heat of vaporization, J/g	445.59	509.88	309
Heat sublimation, J/g	507.39	602.44	-
Heat of combustion (low), kJ/g	119.93	50.02	44.5
Heat of combustion (high), kJ/g	141.86	55.53	48
Specific heat (C) of NTP gas, J/g-K	14.89	2.22	1.62
Specific heat (C) of NBP liquid, J/g-K	9.69	3.50	2.20
Specific heat ratio (Cp/Cv) of NTP gas	1.383	1.308	1.05
Specific heat ratio of NBP liquid	1.688	1.676	-
Viscosity of NTP gas, g/cm-s	0.0000875	0.000110	0.00052
Viscosity of NBP liquid, g/cm-s	0.000133	0.001130	0.002
Thermal conductivity of NTP gas, mW/cm-K	1.897	0.330	0.112
Thermal conductivity of NBP liquid, mW/cm-K	1.00	1.86	1.31
Surface tension of NBP liquid, N/m	0.00193	0.01294	0.0122
Dielectric constant of NTP gas	1.00026	1.00079	1.0035
Dielectric constant of NBP liquid	1.233	1.6227	1.93
Index of refraction of NTP gas	1.00012	1.0004	1.0017
Index of refraction of NTP liquid	1.110	1.2739	1.39
Adiabatic sound velocity in NTP gas, m/s 1294	1294	448	154
Adiabatic sound velocity in NBP liquid, m/s	1093	1331	1155
Compressibility factor (Z) in NTP gas	1.0006	1.0243	1.0069

APPENDIX A: Physical and Chemical Properties of Hydrogen, Methane and Gasoline (Continued) *** (Ref. 1)

PROPERTY	HYDROGEN	METHANE	GASOLINE
Compressibility factor (Z) in NBP liquid	0.01712	0.004145	0.00643
Gas constant (R), cc-atm/g-K	40.7037	5.11477	0.77
Isothermal bulk modulus ( ) of NBP liquid, MN/sq.m	50.13	456.16	763
Volume expansivity ( ) of NBP liquid, 1/K	0.01658	0.00346	0.0012
Limits of flammability in air, vol. %	4.0 - 75.0	5.3 - 15.0	1.0 - 7.6
Limits of detonability in air, vol. %	18.3 - 59.0	6.3 - 13.5	1.1 - 3.3
Stoichiometric composition in air, vol. %	29.53	9.48	1.76
Minimum energy for ignition in air, mJ	0.02	0.29	0.24
Autoignition temperature, K	858	813	501-744
Hot air-jet ignition temperature, K	943	1493	1313
Flame temperature in air, K	2318	2148	2470
Percentage of thermal energy radiated from flame to surroundings, %	17 - 25	23 - 33	30 - 42
Burning velocity in NTP air, cm/s	265 - 325	37 - 45	37 - 43
Detonation velocity in NTP air, km/s	1.48 - 2.15	1.39 - 1.64	1.4 - 1.7
Diffusion coefficient in NTP air, sq cm/s	0.61	0.16	0.05
Diffusion velocity in NTP air, cm/s	<2.00	<0.51	<0.17
Buoyant velocity in NTP air, m/s	1.2 to 9	0.8 to 6	nonbuoyant
Maximum experimental safe gap in NTP air, cm	0.008	0.12	0.07
Quenching gap in NTP air, cm	0.064	0.203	0.2
Detonation induction distance in NTP air	L/D ~ 100	---	-
Limiting oxygen index, vol. %	5.0	12.1	11.6
Vaporization rates (steady-state) of liquid pools without burning, cm/min	2.5-5.0	0.05-0.5	0.005-0.02
Burning rates of spilled liquid pools, cm/min	3.0 to 6.6	0.3 to 1.2	0.2 - 0.9
Toxicity	nontoxic (asphyxiant)	nontoxic (asphyxiant)	slight (asphyxiant)
Energy of explosion, ** (g TNT)/(g fuel) ~ 24	~ 11	~ 10	
Energy of explosion,** (g TNT)/(cc NBP liquid fuel)	1.71	4.56	7.04
Energy of explosion, (kg TNT)/(cu.m) NTP gaseous fuel)	2.02	7.03	44.22

NBP = normal boiling point
NTP = 1 atm and 20 C (293.15 K)

* Thermophysical properties listed are those of parahydrogen

** Theoretical explosive yields

*** Property values are the arithmetic average of normal heptane and octane in the cases where "Gasoline" values could not be found (unless otherwise noted)

APPENDIX B

Hydrogen Leak and Fire Detection Techniques

Survey of Hydrogen Fire and Leak Detection Practices

Type of facility	LH₂ or GH₂	Inside or outside	Pressure and/or temperature	Capacity and/or usage	Leak check methods	Portable hydrogen detectors (principle)	Fixed hydrogen detectors			Hydrogen fire detectors	Remarks
							Principle	Sampling heads	Number of heads		
Storage	GH₂	Out	2000 and 600 psi	120,000 cu ft (2 trailers)	Soap bubbles when connecting trailers; tape around flanges, look for ruptures or bulges	None	None	....	....	None	Considering hydrogen detection tapes.
Test cell, mixing characteristics	GH₂	In	600 psi	About 0.1 lb/sec	Unperforated tape around flanges, semipermanent leak-detecting system	None	None	....	....	None	
Production and use of hydrogen for catalytic hydrocracking	GH₂	Out	....	Several million cu ft/day	Tape and bubble liquid	Catalytic combustion (2 manufacturers)	None (except tape)	....	....	None	Hydrogen produced is not pure; therefore, flames are somewhat easier to see than pure hydrogen flames. Detectors also used for other combustible gases. Fixed head locations: Squibber, chemistry laboratory, control room, propane compressor, and electrical power room. Alarm at 25 and 40 percent LEL.
Liquid hydrogen facility	Both	Both	From 1900° F at 250 psi to 40.5 R at 10 psi	200,000 gal/day 600,000 gallons storage	Bubble compound and tape with punched holes	Catalytic combustion (2 manufacturers	Catalytic combustion	Aspirated	12	None	
Hydrogen production by hydrogenation processes	GH₂	Both	1600° to 2000° F at about 200 psi, to ambient temperature, 0.4 psi	10 to 15 × 10⁶ cu ft/mo 150,000 cu ft storage	....	Catalytic combustion	None	....	....	None (ultraviolet sensor used as furnace flame monitor)	
Research laboratory	LH₂	In	1 to 5 atmospheres	Few thousand gallons	Portable detectors	Catalytic combustion	Catalytic combustion	Diffusion	≅20	Overhead detectors in building	Warning and alarm concentrations at 4 and 10 percent LEL. Automatic shutdown of experimental electronics near hydrogen and activation of high-speed fans.
Hydrogenation and other processes	GH₂	Both	1 atmosphere to 100 psi; one operation at 3000 psi	30 × 10⁶ cu ft/year. Storage about 50,000 cu ft	Pressure decay and soap bubbles	Ultrasonic	None	....	....	None (sprinkler system in buildings)	
Propulsion laboratory	GH₂ (from LH₂)	Both	GH₂ at 3500 psi	2 × 10⁶ gal/year LH₂ (vaporized); 100,000 gallons storage	....	....	Catalytic combustion	Aspirated	4 or 6 in each room	None	Alarm at 30 percent LEL, if detected by at least two sampling points in a given indoor area. Sampling points in upper part of room.
Heat transfer laboratory	Both	Out (Partially enclosed)	GH₂—up to 3000 psi at 500° F. LH₂—up to 4000 psi	200 gallons, LH₂	Portable detector	Catalytic combustion	None	....	....	None	Flares used in test areas to ignite accidentally escaping hydrogen.
Storage (at least ¼ mile from other facilities)	LH₂	Out	....	28,000 gallons permanent; 150 to 5000 gallons portable dewars	Visual observation of frosting during transfer	None	None	....	....	None	
Storage facility (20 to 500 feet from test facility)	LH₂	Out	....	30,000 gallons	....	....	Catalytic combustion	Diffusion	2	Thermal type triggers deluge system	One sensor over storage tank, one over vent stack.

Survey of Hydrogen Fire and Leak Detection Practices—Continued

Type of facility	LH$_2$ or GH$_2$	Inside or outside	Pressure and/or temperature	Capacity and/or usage	Leak check methods	Portable hydrogen detectors (principle)	Fixed hydrogen detectors			Hydrogen fire detectors	Remarks
							Principle	Sampling heads	Number of heads		
Shock tube research	GH$_2$	In	5000 psi (intermittent)	...	...	...	Catalytic combustion	Diffusion	5	None	Sensor location: (1) one at highest point in room, 12 to 15 feet above equipment; (2) three along tube about 4 inches above it; and (3) one in exhaust vent.
Brazing furnace	GH$_2$	In	~1 psi at 1500° to 2000° F.	5000 cu ft/hr maximum	Bubble compound and portable detector	Thermal conductivity	None	...	...	None	Leaks at high temperature occur in container inside furnaces above autoignition temperature.
Storage	GH$_2$	Out	6000 psi	...	...	None	None	...	...	None	
Propulsion research	Both	Out (Partially enclosed)	...	~250 gallons LH$_2$	Portable detector	Catalytic combustion	Catalytic combustion	Diffusion	4	None	Sensors under roofs at, or near, hydrogen areas.
Production and use of hydrogen for hydrocracking	GH$_2$	Out	...	Millions of cu ft/day	Breaks in plastic tape; portable detectors	Catalytic combustion (2 models)	None	...	...	None	Visual detection of accidental fires; small fires seen at night. Leaks sometimes diluted with steam.
Flame studies laboratory	GH$_2$	In	...	Small	...	...	Catalytic combustion	Diffusion	4	None	Placement: three sensors in laboratory—two in corners (14 feet above floor), one above burner; one sensor in control room.
Storage	LH$_2$	Out	...	200,000 and 30,000 gallons	...	None	None	...	...	None	
Rocket engine test	Both	Out	1500 psi	50,000 gallons	Helium-pressurized bubble compound; portable detector	Catalytic combustion	Catalytic combustion	Diffusion	2	Infrared television	Sensor heads attached to cable; can be moved and repositioned around test facility.
Pump and high-pressure storage	GH$_2$	Out	6000 psi	8-inch by 30-foot bottle	...	None	None	...	...	None	
Shock tube (under construction)	GH$_2$	In	12,000 psi up to 600° K	...	...	...	Catalytic combustion	Diffusion	...	None	
Compressor for pipeline system	GH$_2$	Partially enclosed	6000 psi	...	...	...	Catalytic combustion	Diffusion	4	None	Sensors above compressors and in roof. Replace aspiration-head system.
Rocket engine testing	LH$_2$	Both	...	15,000 gal/mo	...	Catalytic combustion	Catalytic combustion	Aspiration	8	Flame monitor in exhaust scrubber	Sampling points 8 to 100 feet from analyzer: (1) one 10 feet over LH$_2$ run tank; (2) one 12 feet over engine; (3) four in exhaust scrubber; (4) one in fuel pit, and (5) one in GH$_2$ storage pit.
Storage and LH$_2$ vaporizer	Both	Out	...	8000 gallons, plus 20 GH$_2$ bottles (2 by 20 feet)	...	...	Catalytic combustion	Diffusion	3	Thermal detectors trigger extinguisher	Diffusion heads over storage tank, vent stack, and vaporizer.
Production and use of hydrogen for reaction processes	GH$_2$	Both	From 2 to 8 psi at ambient temperature; to 5000 psi at 600° F.	7 × 10^6 cu ft/day 100,000 cu ft storage	...	Catalytic combustion; ultrasonic	Catalytic combustion	Aspiration	4	None	Alarm at 20 percent LEL, automatic shutdown of certain apparatus for a local concentration of 40 percent LEL.

Survey of Hydrogen Fire and Leak Detection Practices—Continued

Type of facility	LH_2 or GH_2	Inside or outside	Pressure and/or temperature	Capacity and/or usage	Leak check methods	Portable hydrogen detectors (principle)	Fixed hydrogen detectors			Hydrogen fire detectors	Remarks
							Principle	Sampling heads	Number of heads		
Launch complex for space vehicles	Both	Out	...	Hundreds of thousands of gallons	...	...	Catalytic combustion	Diffusion	≅164	Ultraviolet fire detectors; G-M tube (about 60); thermal wire at flanges; etc. (42)	Output of each sensor to panels in control center and to event recorder. Hydrogen detectors alarm at 25 percent LEL. Infrared television being considered.
Cryogenic testing of materials, (e.g., open test cells)	LH_2	Both	Ambient pressure	2000 gal/mo	...	Catalytic combustion	Catalytic combustion	Aspiration	6	Ultraviolet sensor (furnace-monitor type) at one enclosed test cell for fire detection	Fixed leak detectors, one above each cell, indicate when area is safe to enter (less than 20 percent LEL).
Rocket engine and structural testing	Both	Out	...	Hundreds of thousands of gallons	...	Catalytic combustion	Catalytic combustion	Diffusion	...	Ultraviolet fire detectors (G-M tube); thermal wire	Only false fire alarm due to welding torch.
Testing of rocket engine at simulated altitude	LH_2	In	...	...	...	...	Catalytic combustion	Aspiration	...	Considering infrared television	
Hydrogenation processes	GH_2	Both	9 to 15 psig and 150 psig	≅20,000 cu ft/hr	Soap bubbles	Ultrasonic; catalytic combustion	None	...	...	None	Some difficulty with ultrasonic detector due to background noise level.
Production and use of hydrogen in hydrocracking and other processes	GH_2	Out	Up to 3000 psi at several hundred °F.	Up to 14 × 10^6 cu ft/day	Tape, tape with holes, and bubble compound	Catalytic combustion	None	...	...	None	Visual detection of fires, usually at night.
Propulsion test cell (combustion studies)	GH_2	In	600 psi	Up to 1 lb/sec for 15 or 20 seconds	...	...	Catalytic combustion	Diffusion	1	Ultraviolet flame detector used to ensure ignition	Rapid air flow causes false alarms from fixed H_2 sensor; helped by wrapping head with asbestos cloth. Head is 10 to 20 feet above and to side of flame area.

APPENDIX C

Bibliography

APPENDIX C: Bibliography

Codes, Standards and Regulations

Advisory Panel on Experimental Fluids and Gases, NASA Lewis Research Centre, Hydrogen Safety Manual, NASA TM-X-52454, 1968.

> Presents acceptable standards and practices, for minimum safety requirements, for most aspects of hydrogen handling and usage, where both personnel and equipment are concerned. Does not cover situations with additional hazards, such as highly congested areas, or with low safety margin.

Air Product and Chemicals, Inc., Liquid Hydrogen Safetygram, Box 538, Allentown, PA. 18105.

> Briefly discusses standards, regulations and guidelines for the safe storage, handling and transport of liquid hydrogen: a four-page folding pamphlet.

American Society for Testing and Materials, Cryogens and Gases: Testing Methods and Standards Development, STP 537.

> This document consists of six papers addressing this problems and standards requirements for gases and cryogens. The areas of concern are frozen foods, vehicle fuel containers, cryogenic propellants and pressurizing gases, LOX/LNG mixtures, design and testing of cryogenic equipment and transport properties of cryogenic fluids.

Canadian Gas Association, Amendment # 1 to CANI-B149.1-M80, Installation of Compressed Natural Gas Fuel Systems and Containers on Highway Vehicles and Requirements fo Refuelling Stations, October 1982.

> Covers the installation of compressed natural gas fuel systems and containers on highway vehicles as well as requirements for compressed natural gas refuelling stations.

Canadian Gas Association, Amendment # 1, to CANI-B149.2-M80, Installation of Propane Fuel Systems and Tanks on Highway Vehicles.

> Covers installation of propane fuel systems and tanks on highway vehicles.

Canadian Gas Association, CGA Preliminary Standard 12.1-1981 Propane Fuel System Components for Use on Highway Vehicles, November 1981.

> This standard applies to the construction and performance of retrofitted propane fuel system components providing motive power of highway vehicles utilizing internal combustion engines.

Canadian Gas Association, CGA Preliminary Standard 12.3-1981 Compressed Natural Gas Fuel System Components for Use on Highway Vehicles, June 1981.

> This standard applies to the construction and performance of retrofitted compressed natural gas fuel system components providing motive power for new or existing highway vehicles utilizing internal combustion engines.

Fuels Safety Branch, Ministry of Consumer and Commercial Relations, Province of Ontario, Propane Standard No. 1/82, Installation of Propane Carburation Equipment and Tanks on Highway Vehicles, March 1982.

> This standard applies to the installation of propane carburation equipment and storage tanks on highway vehicles. It does not include OEM installation of equipment in accordance with Canadian Federal Government Standard MVSS301.

Government of Ontario, Energy Act, Chapter 139, Regulations 288, 289, 290, 291, 292, January 1982.

> Energy regulations legislated in Ontario including the Fuel Oil Code, Gas Pipeline Systems, Gas Utilization Code, Oil Pipeline Transportation Systems and Propane Storage Handling and Utilization Code.

Hord, J., National Bureau of Standards, Hydrogen Safety: An Annotated Bibliography of Regulations, Standards and Guidelines, Int. J. Hydrogen Energy, Volume 5, pages 579-584, Pergamon Press Ltd., 1980.

> This document contains a table of federal, mandatory regulations applicable to the distribution of liquid and gaseous hydrogen and the manufacture and maintenance of hydrogen equipment. A second table of references is presented for non-mandatory standard and guidelines pertinent to hydrogen equipment/facilities specifications and safety.

Ludtke, P.R., National Bureau of Standards, Register of Hydrogen Technology Experts, prepared for NASA, NASA CR-2624, October 1975.

> Presents the names of approximately 235 individuals who are considered experts in various hydrogen related technologies. Approximately 90 organizations are listed. Each person is listed by organizational affiliation, address and principal area of expertise.

Ministry of Government Services, Government of Ontario, Ministerial Responsibility for Acts, Alan Gordon, printer, January 1983.

> A list of Provincial Acts under their designated ministry of responsibility

Minister of Transportation and Communications, Government of Ontario, Bill 93, Dangerous Goods Transportation Act, 1981, Printed by Alan Gordon, Toronto 1981.

> Legislated regulations regarding the transportation of goods designated as dangerous, such as (i) explosives, (ii) compressed, refrigerated, liquefied or pressurized and dissolved gases, (iii) flammable and combustible liquids, (iv) flammable and combustible solids, (v) oxidizing substances, (vi) toxic and infectious substances, (vii) corrosives.

National Fire Protection Association, Codes and Standards, 1983 Catalog.

> Includes: National fire codes, booklets, code related publications, index to the national fire codes library list, ordering information.

Safety Management

Balthasar, W., Schoedel, J.P., Hydrogen Safety Manual - OSGPB84-163468, Corp. Source - Commission of the European Communities, Luxembourg. Journal Vol. - 08410. Report Date - 1983. Report No. - EUR-8396-EN.

> This manual addresses the safety considerations issue by outlining methods, procedures and examples of how to handle hydrogen safely.

Brown, W.J., NASA Lewis Research Centre, Safety Management of Complex Research Operations, Fifth International System Safety Conference, Denver, Co., July 30, 1981.

> A description of the Safety Management Program at the Lewis Research Centre. This program covers potential hazard areas such as high energy fuels, hydrocarbon fuels, high pressure systems, high voltage systems, toxic chemicals, radioactive materials, high speed rotating machinery and high powered lasers.

Custer, R.L.P., Bright, R.G. National Bureau of Standards, Fire Detection: The State-of-the-Art, prepared for National Aeronautics and Space Administration, June 1974, COM-74-50638.

> The current state-of-the-art in fire detection technology is reviewed considering the nature of fire signatures, detection modes used, test methods, performance requirements and code requirements. Also included are present trends in standard development and recommendations for future work.

Edeskuty, F.J., Bartlit, J.R., Carlson, R.V., Stewart, W.F., Cox, K.E., Rider, R., Williams, M., Los Alamos Scientific Laboratory, Hydrogen Safety and Environmental Control Assessment, November 1, 1978 - September 30, 1979, Final Report, LA-8225-PR.

> Safety and environmental concerns regarding the use of hydrogen and its public interactions are identified. A coordinated program for resolving these concerns, containing elements of assessment and analysis for various areas, is set out.

Factors affecting the broadened use of hydrogen - NAS 09-44 76N18661, JJ574450 Jet Propulsion Laboratory, California Instit. of Tech., Pasadena, Calif.

> The future role of hydrogen is considered. Specific factors discussed include: storage, transmission, and distribution problems: materials compatibility and safety: environmental and social implications of increased hydrogen usage: and the economics related to expanding hydrogen use.

Grilly, E.R., Kerr, E.C., Edeskuty, F.J., Stearns, J.G., Burch, C.A., Los Alamos Scientific Laboratory Liquid Hydrogen Safety Committee, Liquid Hydrogen: A Guide for the Safe Handling and Storage of Liquid Hydrogen at LASL Facilities, June 15, 1962.

> This guide treats the very general aspects of liquid hydrogen safety. It refers to some specific examples which should be regarded as illustrative rather than comprehensive. It is assumed that the reader has access to information related to the safety aspects of good housekeeping, chemicals, radioactive sources, equipment handling and transportation hazards, common utilities, etc.

Knowlton, R.E., Chemetics International Company, An Investigation of the Safety Aspects in the Use of Hydrogen as a Ground Transportation Fuel.

> This paper outlines the strategy, hazard identification approach and the results achieved when potential systems for the transmission, storage, distribution and refuelling of hydrogen were subjected to the hazard identification procedure. Selected scenarios have specific reference to an LH_2 refuelling station.

Knowlton, R.E., Chemetics International Ltd., An Introduction to Hazard and Operability Studies, The Guide Word Approach, February 1981.

> An introduction to the "guide word" technique of hazard and operability studies in the process industry. This method comes from the detailed plant design where images of deviations are generated by the use of guide words to stimulate a schematic search for possible hazards and operational difficulties.

Knowlton, R.E., Imperial Chemical Industries Limited, Hazard and Operability Studies and their initial applications in research and development, Research and Development Management, Vol. 7, No. 1, October 1976, Ed. A.W. Pearson.

> Describes an approach to operations safety in the process industry in addition to an extension of the method into the research and development area.

Knowlton, R.E., Chemetics International Company, Hydrogen Safety, an assessment of the safety problems associated with the use of hydrogen as a ground transportation fuel, Draft Final Report, Book 1 and 2, prepared for the National Research Council of Canada, January 1983.

> This document is concerned with transmission, distribution and storage of hydrogen as a gas or cryogen liquid. Schematic designs for systems of this type are created and subjected to hazard and operability studies. Hazards are identified and recommendations are made to eliminate, control or contain them.

Krupka, M.C., Edeskuty, F.J., Stewart, W.F., Williamson, K.D., Los Alamos National Laboratory, A Guide for the Safe Use of Hydrogen, prepared for the Urban Transportation Development Corporation, Report 325-CR-701-105

> This is a safety guide for the use of liquid and gaseous hydrogen during the design, development, test and manufacture stages of a hydrogen-fuelled transit vehicle.

Liquefied gaseous fuels safety and environmental control assessment program progress report - NAS 05-28 80N14266 DM226776 Department of Energy, Washington, D.C. Cont. No.: EP-78-0-03-2057, EP-78-0-05-6020, EP-78-0-02-4734, EE-77-S-02-4204, EE-77-S-02-4447, EE-77-S-02-4548, EY-76-0-06-1830. RPT. No.: DOE/EV-0036. AVAIL NTIS 725 P. HC A99/MF A01

> Research is reported on the safety and environmental aspects of liquefied gaseous fuels including natural gas, petroleum gas, hydrogen and ammonia. Spills and fires are among the handling, storage and transportation hazards assessed.

Process Safety Management (Control of Acute Hazards) - Chemical Manufacturers Association, 2501 M Street, NW, Washington, DC 20036. May 1985.

> This document compares the various methods available for process hazard identification and assessment. The various steps in designing, commissioning and operating a facility are also described. Application of the hazard identification technique known as "Hazard and Operability Studies" (HAZOP) to a conceptual hydrogen pumping station is illustrated.

Schmucker, R., Safety Aspects of a Widespread hydrogen energy economy - NAS 06-31 78A18857, International Workshop on Hydrogen and its perspectives, Liege, Belgium, Novemeber 15-18, 1976, Proceedings, Volume 2. In French.

> Profitability constraints on safety considerations in a widespread hydrogen energy economy are discussed. Hydrogen uses and possible human contact are examined with attention to the ignition and combustion characteristics of hydrogen. Three approaches to safety are urged - education, improvement of safety procedures, and passive means.

Theyskens, A., Aspects relative to security and environment in the production and use of hydrogen in the new Esso refinery at Antwerp - NAS 06-44 78A18854, International Workshop on hydrogen and its perspectives, Liege, Belgium, November 15-18, 1976, Proceedings. Volume 2. (A78 - 18826 06-44). In French. Corp. Auth-Esso Belgium, Antwerp, Belgium.

Hydrogen Properties and Associated Hazards

Arthur D. Little Inc., Final Report, Electrostatic Hazards Associated with the Transfer and Storage of Liquid Hydrogen, prepared for NASA, George C. Marshall Space Flight Centre, May 1961, C-61092.

> This report summarizes the results of an experimental program to investigate the potential hazards of static charge generation and accumulation in well-grounded liquid hydrogen storage and transfer systems.

Baker, W.E., Parr, V.B., Bessey, R.L., Cox, P.A, Southwest Research Institute, Assembly and Analysis of Fragmentation Data for Liquid Propellant Vessels, prepared for NASA Lewis Research Centre, NASA CR-134538.

> This document assembles and analyses fragmentation data for exploding liquid propellant vessels. The report presents methods which allow the prediction of fragment patterns, given the type and quantity of propellant, type of accident and other parameters.

Edeskuty, F.J., Safety Chapter, Hydrogen: Its Technology and Implications, Volume II, Transmission and Storage of Hydrogen, CRC.

> A discussion of hydrogen properties, related hazards and avoidance of hazards in the design and operation of systems which store, handle and transport hydrogen.

Edeskuty, F.J., Safety - NAS 02-28 81A11756, Hydrogen: Its Technology and Implications. Volume 4. (A81-11751 01-44) Boca Raton, Fla., CRC Press, Inc., 1979 P. 203-219, ERDA-Sponsored Research. Corp. Auth-California, University, Los Alamos, N. Mex.

> A review is presented of safety considerations in hydrogen operation, design of equipment, operator training, and codes and regulations. Properties of hydrogen including its flammability, detonation range, flame emissivity, and heat of vaporization are discussed; hazards of combustion within closed spaces and the weakening of structural equipment by embrittlement are described. Avoidance of hazards by purging air prior to operation, ventilation of the surrounding areas and avoidance of leakage are illustrated; regulatory codes must consider the thermal contraction of materials of construction which contain LH2.

Hord, J., U.S. Department of Commerce, National Bureau of Standards, Correlations for Predicting Leakage Through Closed Valves. NBS Technical Note 355, R-433, August 1967.

> The correlation of parameters toward the prediction of leakage of fluids across valve seats, welded and threaded fittings, seals, etc. Various formulae are examined, and two methods of correlating leakage for single phase fluids are deduced.

Hord, J., U.S. Department of Commerce, National Bureau of Standards, Explosion Criteria for Liquid Hydrogen Test Facilities, NBS Report 10734, U-227, February 1972.

> This document reviews current practices for assessing personnel safety hazards at hydrogen test facilities. Hydrogen/air explosion data are reviewed. Other considerations are fireball and over pressure hazards, shrapnel hazards.

Hord, J., Is Hydrogen a Safe Fuel? International Journal of Hydrogen Energy, Volume 3, Pages 157-176, Pergamon Press, 1978.

> The safety aspects of hydrogen are examined and compared with those of methane and gasoline. Physical and chemical property data for the three fuels are used as a basis for comparison. The safety aspects considered are fire hazard, fire damage, explosive hazard and explosive damage.

Joint Army, Navy, NASA, Air Force, Propulsion Committee, Hazards Working Group, Hazards of Chemical Rockets and Propellants Handbook, Volume III, Liquid Propellant Handling, Storage and Transportation, AD870259, May 1972.

> This document provides safety criteria, procedures, instructions, precautions and technical guidelines to assist in the minimization of hazards associated with the handling, storage, transport and use of liquid propellants.

McCarty, R.., Weber, L.A., U.S. Department of Commerce, National Bureau of Standards, Thermophysical Properties of Parahydrogen from the Freezing Liquid Line to 5000 R for Pressures to 10,000 Psia, NBS Technical Note 617, R-701, 1972.

The tables include entropy, enthalpy, internal energy, density, volume, speed of sound, specific heat, thermal conductivity, viscosity, thermal diffusivity, Prandtl number and dielectric constant for 65 isobars. In addition, tables for saturated vapour and liquid including the above properties plus surface tension, are given.

Mccarty, R.D., Hord, J., Roder, H.M., NG263089, Selected Properties of Hydrogen (Engineering Design Data) final report - NAS 24-25 81N33266, National Bureau of Standards, Boulder, Co., Rpt. No.: PB81-211492 NBS-MN-168 LO-800600195 Avail NTIS 525 p. HC A22/MF A01

Data on hydrogen properties research are presented. Thermophysical properties of liquid, liquid vapour, vaporous and gaseous hydrogen are presented and the solid-liquid, solid vapour, and solid phase properties are compiled. Ortho para modifications of the hydrogen molecule and attendant property variations are considered. Combustion and safety data, pertinent to hazard analysis of hydrogen systems, and miscellaneous properties are collected. Data figures, data tables, and symbols, units, and conversion factors are summarized.

McKinley, Clyde., Safe handling of hydrogen - EIX 80-12 02349, ACS Symp Ser N 116, Hydrogen: Prod. and Mark., based on a symp at the ACS. CSJ (Am. Chem Soc/Chem Society of Japan) Chem Congr. Honolulu, Hawaii. Published by ACS, Washington, DC, 1980.

The Physical/Chemical properties of hydrogen which control hydrogen handling hazards are summarized. Hazards specifically discussed are gaseous hydrogen fires and explosions, liquid hydrogen explosions, "cold burns", embrittlement of handling systems resulting from low temperatures, bursting of equipment through evaporation of confined liquid hydrogen, and oxygen deficient breathing atmospheres. Criteria which may be used for hazard review of practices and procedures to control or avoid the listed hazards are provided.

Reider, R., Edeskuty, F.J., Hydrogen safety problems - NAS 14-44 77A33402, 1st World Hydrogen Energy Conference, Miami Beach, Fla., March 1-3, 1976, Proceedings. Volume 3. (A77-33326 14-44) Coral Gables, Fla. Corp. Auth- California, University, Los Alamos, N. Mex.

> Hazardous situations are discussed in terms of impurities. Hydrogen combustion characteristics, asphyxiation and unconfined and confined hydrogen/air deflagrations. Effects of cryogenic hydrogen are assessed relative to pressure buildup, condensation, oxygen enrichment, and cold injury.

U.S. Department of Commerce, National Bureau of Standards, Thermophysical Properties Division, List of Publications, Supplement No. 1, September 1977 to October 1978.

U.S. Department of Commerce, National Bureau of Standards, Thermophysical Properties Division, List of Publications, Supplement No. 2, November 1978 to October 1979.

U.S. Department of Commerce, National Bureau of Standards, Thermophysical Properties Division, List of Publications, Supplement No. 3, November 1979 to December 1980.

U.S. Department of Commerce, National Bureau of Standards, Thermophysical Properties Division, List of Publications, Supplement No. 4, January 1981 to April 1982.

Voth, R.O., Safety of Hydrogen Pressure Gauges, Advances in Cryogenic Engineering, F-2, Volume 17, Plenum Press, New York, 1972.

> This study documents a study of the safety of various gauge case designs for use in high pressure gaseous hydrogen systems. Damage due to fire and debris from gauge rupture was considered in the context of personnel safety.

Weintraub, A.A., United States Atomic Energy Commission, Control of Liquid Hydrogen Hazards at Experimental Facilities: A Review, HASL-160,May 1965.

> A discussion of the properties of hydrogen are presented above with designated materials for liquid hydrogen systems. Liquid hydrogen hazards at experimental facilities and associated control techniques are presented.

Zabetakis, M.G., Burgess, D.S., Research on the Hazards Associated with the Production and Handling of Liquid Hydrogen, report of investigations 5707, United Sates Department of the Interior, Bureau of Mines, 1960.

> This report describes theoretical and experimental results of investigations related to the handling of liquid hydrogen. The conclusion and recommendations discuss the elimination of hazards associated with (i) the formation of shock-sensitive condensed liquid hydrogen/solid oxygen mixtures and (ii) fires.

Zabetakis, M.G., Safety with Cryogenic Fluids, The International Cryogenics Monographic Series, General Ed., Dr. K. Mendelssohn, Dr. K.D. Timmerhaus, Plenum Press, 1967.

> The referenced portion of this document is Chapter 2, Physiological Hazards. The hazards considered are those associated with human exposure to cryogenic fluids and their vapours. These are catagorized under frostbite, respitaory ailments, and miscellaneous effects.

Zalosh, R.G., Factory Mutual Research Corporation, Comparative Analysis of Hydrogen Fire and Explosion Incidents, Quarterly Report No. 1, prepared for Division of Operational and Environmental Safety, U.S. Department of Energy, COO-4442-1, December 1977.

> This is the first of a series of reports which will conduct a comparative analysis of the safety records of hydrogen and natural gas, identify hydrogen safety aspects, further research and standards/codes modification and quantitatively assess the relative hazards of alternative modes of hydrogen storage, transport and utilization and disposal. In this report, available sources of hydrogen and natural gas accident data are described.

Cryogenic Systems

Faure, A., Safety problems in the use of Liquid Hydrogen - NAS 06-31 78A18858, International workshop on hydrogen and its perspectives, Liege, Belgium, November 15-18, 1976, Proceedings, Volume 2. Corp. Auth- L'Air Liquide, Paris, France.

> Cryogenic and combustion hazards associated with the use of liquid hydrogen are examined. Cryogenic hazards include contamination by condensed air, excessive pressures, damage to exposed materials, and human tissue destruction. Procedures are considered for avoiding the formation of flammable mixtures in liquid hydrogen containers or in the atmosphere, and for avoiding ignition sources. Safety features for storage sites and methods of fighting hydrogen fires are discussed.

Frizen, D.J., Mondenhall, J.R., National Bureau of Standards, Publications and Services of the Cryogenics Division, National Bureau of Standards 1953-1977, NBS Technical Note 1005, April 1978.

> This document catalogues publications and services of the Cryogenics Division, along with author and subject indices for the period 1953 to 1977. In addition, it contains a listing of available thermodynamic properties, charts, bibliographies, and miscellaneous reports of cryogenic interest.

Makeev, V.I. Pleshakov, V.F. Chugev, A.P., Fizika Goreniia I Vzeyva,Formation and combustion of hydrogen-air mixtures during liquid hydrogen evaporation into the atmosphere - NAS 05-25 82A16266, Vol. 17, Sept.-Oct. 1981,
p. 14-21. In Russian.

> Concentrations and temperatures have been measured during liquid hydrogen evaporation under stationary conditions. A relationship is established between the excess enthalpies and mass concentrations corresponding to the conditions of free turbulent mixing. Empirical expressions are derived which relate the turbulent mixing coefficient to the Reynolds number. The extents of concentration zones presenting explosion of fire hazard are determined.

Safety panel of the British Cryogenics Council, Cryogenics Safety Manual, A Guide to Good Practice, Second Edition, Mechanical Engineering Publication, Ltd., London, 1982.

> This document attempts to provide guidance to those concerned with the operation, maintenance and supervision of plants producing, storing and handling various commercial gases at cryogenic temperatures. It deals with health, safety and hazard control.

Timmerhaus, K.D., Flynn, T.M., Safety with Cryogenic Systems, R-2, Advances in Cryogenic Engineering, Proc., Cryogenic Engineering Cont., Volume 23, Plenum Press, New York, 1978.

> A summary and discussion of characteristics and control of hazards associated with cryogenic systems, such as physiological materials and construction, flammability and explosion and high pressure gas hazards. Also included is a brief treatment of general safety principles.

Safety: Application Specific

Bain, A.L., NASA Space Program Experience in Hydrogen Transportation and Handling, Int. J. Hydrogen Energy, Vol. 1., pp. 173-188, Pergamon Press, 1976.

> This paper presents the experience gained in the transportation and handling of hydrogen in support of the Apollo launch site. It reveals the types of systems involved in handling hydrogen, safety practices, operational techniques and general experience gained over the years.

Brewer, G.D., Some environmental and safety aspects of using hydrogen as a fuel - NAS 07-44 79A20774, (Commission of the European Communities, Euratom Course, Ispra, Italy, May 9-13, 1977) International Journal of Hydrogen Energy, Vol. 3, Dec. 11, 1978, p. 461-474. Corp. Auth. Lockheed-California Co., Burbank, Calif.

> The use of hydrogen as a fuel for road vehicles and for aircraft is discussed from the viewpoint of environmental and safety considerations. The current pattern of hydrogen use in industrial processes is described, and the use of hydrogen for energy transmission and for household appliances is considered. The problem of air pollution from aircraft is examined.

Corneil, H.G., Heinzelmann, F.J., Nicholson, E.W.S., Exxon Research and Engineering Co., Hydrogen in Oil Refinery Operations.

> Contains a description of hydrogen uses in petroleum refining, projected hydrogen requirements, projected energy prices and the economics of manufacturing refined hydrogen.

Edeskuty, F.J., Safety of liquid hydrogen in air transportation - NAS 07-31
80N16236, L4453961, Los Alamos Scientific Lab., N. Mex., Cont. No.: W-7405-ENG-36, RPT-NO.: LA-UR-79-1416, CONF-790942-1. Avail NTIS 18P. HC A02/MF A01

> The safety factors and problems associated with the use of liquid hydrogen as an aircraft fuel are discussed.

Edeskuty, F.J., et al, Los Alamos Scientific Laboratory, Critical Review and Assessment of Problems in Hydrogen Energy Delivery Systems, Initial Report, August 1978, LA-7405-PR.

This document addresses the potential problem areas associated with the delivery of hydrogen in large quantities, over long distances. The focus is on LH_2 highway transport and GH_2 pipeline transmission. The report treats risk analysis, hydrogen embrittlement and existing regulations and guidelines.

Edeskuty, F.J. Shehan, N.N., et al, Los Alamos Scientific Laboratory, Critical Review and Assessment of Environmental and Safety Problems in Hydrogen Energy Systems, May 1979, LA-7820-PR.

. A review and assessment of environmental and safety problems anticipated in the use of hydrogen as an energy carrier. The report treats such issues as transmission of hydrogen by gas pipeline, shipment of liquid hydrogen, hydrogen embrittlement, codes, standards and regulations and environmental considerations.

Escher, W.J.D., Escher Technology Associates, Survey of Liquid Hydrogen Container Techniques for Highway Vehicle Fuel System Applications, prepared for U.S. Department of Energy, November 1978.

Representative projects for the onboard storage of liquid hydrogen are surveyed world wide. Four cryogenic hydrogen container systems for application to highway vehicles, are evaluated. The documentation of these was intended to provide an information base for further work in this field.

Kelley, J.H., Hagler, R., Storage, Transmission and Distribution of Hydrogen, Int. J. Hydrogen Energy, Vol 5, pp. 35-54, Pergamon Press Ltd., 1980.

Current practices and future requirements for the storage, transmission and distribution of hydrogen are discussed and analyzed to identify inadequacies which must be corrected in order for hydrogen utilization to achieve full potential as a fuel.

McHugh, Manus III, Hydrogen distribution safety - EIX 80-12 02351, ACS symp ser N 116, hydrogen: Prod and Mark, based on a symposium at the ACS/CSJ (Am Chem Soc/Chem. Society of Japan) Chem. Congr. Honolulu, Hawaii. Apr. 2-6 1979. Published by ACS, Washington, DC, 1980 p. 253-275.

> The Industry has enjoyed an enviable safety record in the transport of liquid hydrogen. This paper discusses the safety considerations built into the trailers. For ease of reference, air products trailers and equipment is used to illustrate the safety measures provided for the safe distribution of liquid hydrogen.

Miller M., Safe Handling of Hydrogen in Large Quantities, Proc. International Symposium, Hydrogen in Air Transportation, Sept. 1979, Stuttgart, Germany.

> Addresses safe handling of hydrogen intended for use as a propellant for rocket engines. Concerns such as supply and feed systems, transport and handling, safety measures, incidents and specific laboratory requirements are discussed.

Mueller, M., Safe handling of hydrogen in large quantities - NAS 15-28 80A37337. Hydrogen in Air Transportation: Proceedings of the International symposium, Stuttgart, West Germany, September 11-14, 1979. (A80-37330 15-44) Corp. Auth- Messerschmitt-Boelkow-Blohm GmbH, Ottobrunn, West Germany

> Safe handling of hydrogen which is used as a propellant in rocket engines is examined. Several accidents involving a hydrogen leak, explosions, and failures of electronic equipment leading to accidents were described.

Nezer, C., Safety in hydrogen transport and storage installations - NAS 06-31 78A18856, Nezer, C., International workshop on hydrogen and its perspectives, Liege, Belgium, November 15-18, 1976, Proceedings. Volume 2. (A78-18826 06-44) In French, Corp. Auth.-Association Vincotte, Brussels, Belgium.

> Properties of hydrogen gas and liquid are described, and safety procedures for handling hydrogen are discussed. Procedures for avoiding the formation and ignition of hydrogen-air mixtures are examined; these procedures can involve purging equipment, avoiding and detecting contamination and avoiding electric sparks. The storage of hydrogen gas in subterranean caves is considered.

Rieder, R., Edeskuty, F.J. Hydrogen Safety Problems, International Journal of Hydrogen Energy, Pergamon Press, 1979.

> Addresses hazardous situations and incidents for gaseous and cryogenic hydrogen in the context of its use as a fuel.

The Institute for Hydrogen Systems, Thermochemical Technologies Division, Hydrogen Safety in the Research and Development Environment, October 1984. Report No. IHS-84-19, prepared for the Ontario Ministry of Energy.

Youngblood, W.W., Safety Criteria for the Operation of Gaseous Hydrogen Pipelines Final Report - NAS 03-31 86N12392. Wyle Labs., Inc., Huntsville, Ala. Contract No.: DTRS56-81-C-00043, Report No.: PB85-206159 WR-84-24 RSPA/DMT 10-85/1. Avail NTIS HC A05/MF A01.

> This report discusses the safety criteria for the transportation of gaseous hydrogen by pipeline. Major emphasis is placed on transmission pipelines, but distribution pipeline is also considered. The report concludes that under certain conditions gaseous hydrogen could pose public safety hazards that are not adequately addressed by current safety code regulations.

Zalosh, R.G., Bajpai, S.N., Hydrogen Microscopic Hazard Evaluation - NAS 15-44 82N24706.

> Progress on a preliminary hazard evaluation of hollow glass microspheres for hydrogen transport and storage is reported. The flammability and explosibility of representative hydrogen filled microspheres was assessed. Safety codes and government regulations pertinent to hydrogen filled microspheres are also reviewed.

Hazard Studies

Bollinger, L.E., Fong, M.C., Laughrey, J.A., Edse, R., Experimental and Theoretical Studies on the formation of Detonation Waves in Variable Geometry Tubes, NASA Technical Note D-1983, June 1963.

> A study of detonation induction distances obtained experimentally for hydrogen/oxygen mixtures of 45, 66.67 and 75 per cent hydrogen at initial pressures of 1 and 5 atmospheres in a detonation tube of variable internal geometry.

Jacobs, R.B., Buckley, W.L., Rhodes, J.C., Speer, T.L., Standard Oil Company, The Destruction of a Large Refining Unit by Gaseous Detonation, Chemical Engineering Progress, Volume 53, No. 12, Dec. 1957.

> A descriptive account of explosions occurring within a reactor vessel and high pressure separator at Whiting, Indiana. Also included is an account of damages sustained. The deterioration was initiated by a flammable mixture of O_2 and Naphtha.

Kuchta, J.M., Cato, R.J., Martindill, G.H., Gilbert, W.H., Ignition Characteristics of Fuels and Lubricants, Bureau of Mines Technical Report AFAPL-TR-66-21, March 1966.

> This documentation presents a technical summary of the work which was conducted during a three-year investigation of the ignition, flammability and oxidation characteristics of hydrocarbon combustibles in various nitrogen-oxygen atmospheres.

Ordin, P.M., Review of hydrogen accidents and incidents in NASA operations - NAS 01-44 75A10539, 9th Intersociety energy conversion engineering conference, San Francisco, Calif., August 26-30, 1974, Proceedings. Corp. auth- NASA, Lewis Research Center, Cleveland, Ohio.

> Safety as a major factor in the development of a power economy based on hydrogen produced by nuclear - or solar - energy operated water electrolysis, is considered in terms of the safety problems involved in the production, handling, transportation, and use of liquid and gaseous hydrogen. These problems are reviewed through the records of accidents and incidents that have occurred in the development and operation of NASA's propulsion and power systems. Areas of research and development are suggested for increased safety and for the development of techniques to reduce the consequences of any mishaps.

Randall, P.N., Bland, J., Dudley, W.M., Jacobs, R.B., Effects of Gaseous Detonations upon Vessels and Piping, Chemical Engineering Progress, Vol 53, No. 12, December 1957.

> This article presents work done in the investigation of an explosion which destroyed a refinery at Whiting, Indiana. It considers the principles involved in the rupturing of pipes and vessels by gaseous detonation and gives pertinent engineering and metallurgical information in relation to the explosion.

Sherman, M.P., Hydrogen flame acceleration and transition to detonation - ERDA 8412-012829, 12th Water reactor safety research information meeting, Gaithersburg, Md, USA, 23 Oct 1984, Date: 1984, Report No.: Sand--84-20780, corp. Sandia National Labs., Albuquerque, NM (USA).

> This paper describes the results obtained from two large experimental facilities built at Sandia National Laboratories in Albuquerque, NM.

Stewart, R.D., Aerospace Safety Research and Data Institute, NASA Lewis Research Centre, A Method for Defining Down-Wind Evacuation Areas for Transportation Accidents Involving Toxic Propellant Spills, NASA TM X-68188, 1972.

> Evacuation areas for accidental spills of toxic propellants along rail and highway shipping routes are defined. They are based on current best estimates of propellant evaporation rates from various areas of spill puddles.

Strehlow et al., University of Illinois, The Characterization and Evaluation of Accidental Explosions, prepared for NASA Lewis Research Centre, NASA CR 134779, June 1975.

> A comprehensive review of current standing of accidental explosions. Explosions are characterized by type and their characteristics are discussed.

Varpie, M., Wolfhord, H.G., United States Bureau of Mines, Ignition by Hot Gases, BUM-30-R, August 1960.

> An investigation of the factor affecting ignition of explosive gaseous mixtures by jets of hot gases. Includes description of experimental procedure amid results such as the influence of jet diameter, jet temperature, contact time and miscellaneous observations.

Windgassen, K.F., Kesten, M., Investigation of the hydrogen susceptibility of steels used for the storage and transportation of gaseous hydrogen. Comparison of different testing methods - ERDA 8403-602917, Date: 1983, Report No: EUR--8690-DE, in German. Availability: Commission of the European Communities, Luxembourg.

> The presented work is part of a joint research project carried out by the three companies L'Air Liquide, Hoechst and Messer Griesheim, the general purpose of which was to study the hydrogen susceptibility of commonly used pressure vessel steel grades in order to qualify these materials and to ensure their safe and economic use when handling high pressure hydrogen gas. The particular aim of the research activities presented in here was to provide basic information on the critical condition necessary to initiate hydrogen induced fatigue cracks at possible surface defects.

Zalosh, R.G., Short, T.P., Compilation and analysis of hydrogen accident reports. Final technical report. - USGCOO-4442-4, Corp. Source- Factory Mutual Research Corp., Norwood, MA. Journal Vol. - U7925 N0400 report date- Oct. 78

> Over 400 reports of accidents involving hydrogen have been collected from a variety of sources including insurance companies, government agencies, trade associations, fire protection associations, and individual companies using hydrogen. Most of the accidents occurred in industrial facilities in the period 1965-1977. Representative case histories and tabulations of the data according to the causes and contributing factors are presented. The data indicate that hydrogen explosions have been a more serious problem than other types of hydrogen accidents in terms of the number of incidents, casualties, and reported property damage. Many of the explosions have resulted from undetected accumulations of hydrogen due to leaks, inadequate purging, inadequate ventilation, and obstructed vent systems. The need for special fire and explosion protection measures because of flammability differences between hydrogen and conventional fuels has been reflected in the accident data. Recommendations are presented for improving hydrogen fire/explosion protection technology in the areas of hydrogen detection, emergency high-speed pressure relief devices and explosion venting. (ERA citation 04:042500)